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The Quantitative Determination of Starch As Sizing

By B. X. HERMAN

THE tremendous quantities of starches which are consumed in the textile industry as stiffening and bodying agents are well known. A perusal of textile analytical methods, surprisingly indicates that there has been little published information in this country regarding an accurate determination of starch in textiles as sizing. In England, however, during the past few years work has been carried out in presenting an accurate determination.

The A. A. T. C. C. Sub-Committee on the Determination of Sizing and Finishing Materials in Textiles will welcome this paper as a valuable contribution to the rather scant literature relating to the Quantitative Determination of Finishing Materials in Textiles. The author of this paper, also Mr. R. W. Hook the chairman of the above mentioned committee, will welcome any criticisms or suggestions which readers of the Reporter may be able to contribute upon this subject.
L. A. O.

This determination is not an easy one insofar as, the principal use of starch is that of a finishing material, and in this respect is not always employed *in situ,* but also in combination with other materials, such as glycerin, gums, and gelatins; the last, of course, being utilized where specific handles and feels are desired. The latter materials tend to offset the accuracy of the starch determination.

In the majority of standard textile analyses, a sizing recommendation is given, such as that of Griffin ("Methods of Analysis," P. 372, 1st Ed. 1921, McGraw-Hill).

The procedure outlines the boiling of a dehydrated sample of the sized material in water for ten minutes and then digesting it at 60° C in a diastafor solution for two hours. The sample is then boiled again in distilled water for one hour, washed and dried at 100°C and weighed. The total loss is then computed. This is an analysis prescribed for the determination of sizing consisting of starch and dextrines.

A second procedure for the analysis of sizing materials consists of a thorough boiling in 1% (or under) concentration of hydrochloric acid. That which is removed in this determination includes other finishing materials besides starches.

There are indirect methods for determining finishing materials by first determining the amounts of all other materials present and then computing the amount of finishing materials present by difference.

The standard specifications of the American Society for Testing Materials (A.S.T.M. Standards, 1930) describe their method for sizing determination as follows:—

A dehydrated sample dried to a bone dry weight is boiled for thirty minutes in ½% HCl solution, removing, rinsing in water, followed by boiling in 1% Na_2CO_3 solution. This sample is rinsed again and dried to a constant weight. The loss in weight is calculated, and after an allowance of 3.2% is made for the extracted oils, waxes, and foreign matter, the final difference is returned as percentage size.

Analytical methods as those described in the foregoing may be complete for cotton fabrics in the grey or bleached. However, when we consider heavy woolen or union textile materials which may be processed from shoddy stocks and subsequently sized with various starches, then the inadequacy of the above determinations is evident. The presence of dye in the raw material as well as substances of fine fibrous nature and compounds soluble in the solutions as prescribed in the procedures are factors which would offset the results.

Secondly, starch may be the only finishing material added to the above described type of textile fabric by a manufacturer, and a starch determination might be one of the requisites necessary to comply with certain specifications.

Obviously the analytical procedures described heretofore would be out of the question because of their inaccuracy. The latter statement has been proven to be true when materials made from shoddy stocks which qualitatively were found to be starch free, tested as high

as a 4% loss, when subjected to a hydrochloric acid treatment as described in the foregoing. Consequently, the most plausible course would be to effect the removal of starch in the simplest manner, followed by its quantitative determination. The property of the majority of commercial starches in being hydrolyzed to dextrose and glucose by the action of heat, an enzyme, or an acid, and the subsequent reducing action of the sugar upon an alkaline copper solution has offered the best course for producing an accurate determination.

The purpose, therefore, of this paper is to present (1) a short resumé of analytical procedure for the quantitative determination of starch in textiles and in other industries which utilize starch and (2) to advance a new method for this determination based upon the use of Benedict's modification of Fehling's solution.

In the latter development, the writer is indebted to the kindly advice of Mr. M. A. Kaplan, B.S.M.S.M.D. of the Physiological Chemistry Department of the University of Illinois School of Medicine.

Before proceeding further, the writer recognizes any criticism that all starches do not hydrolize to form reducing sugars. In the main, however, it will be found that the majority of commercial starches undergo this reaction as has been shown by the acid hydrolizations carried out by Fargher and Lecomber (Jour. Text Inst. 22, T. 475, 1931).

Percentage of Starch calculated by acid hydrolysis

Commercial Sago	97.3%
Tapioca Starch	96.5%
Wheat Starch	96.8%
Maize Starch	97.4%
Rice Starch	96.1%

Method for Foodstuffs

Quantitative determinations for starches are numerous in the analyses of foodstuffs, and these may be applicable to textiles. We are presenting a brief outline of determinations of this type accepted officially by the Association of Official Agricultural Chemists (2nd Edition 1924) and are presenting these more in detail since we are of the opinion that they will prove of use to the textile chemist for further study.

A dry 3 gram sample of the test material (in this case, starch) is placed in 50cc. of water, stirred for one hour, transferred to a filter and washed with 250cc. of cold water. The residue is heated for 2.5 hours with 20cc. of HCl (sp. gr. 1.125) diluted with 200cc. of H_2O in a flask provided with a reflux condenser. The flask is then cooled and nearly neutralized with NaOH. The starch is thusly converted to a reducing sugar-dextrose.

Soxhlet's modification of Fehling's solution is then prepared as follows: (a) Copper sulfate solution: Made by dissolving 34.639 grams of $CuSo_4.5H_2O$ in water and diluting to 500cc. (b) Alkaline tartrate solution made by dissolving 173 grams of Rochelle Salts and 50 grams of NaOH in water and diluting to 500cc.

25cc. of each of these solutions are transferred to a beaker and 50cc. of the reducing sugar solution added and the beaker heated to the boil and the boiling continued for exactly two minutes. The solution is then immediately filtered through an asbestos filter in a Gooch crucible with the aid of suction. The precipitate is then washed thoroughly with warm water. In the foregoing procedure, the alkaline cupric copper solution is reduced by the reducing sugar-dextrose-to cuprous oxide.

The reduced copper may then be determined in either of three ways:—(1) Direct weighing of cuprous oxide.

The precipitate in the Gooch crucible after a thorough washing with hot water, is washed with 10cc. of alcohol followed by 10cc. of ether. The precipitate is dried for thirty minutes at 100°C, cooled and weighed.

Previous to the above determination, the Gooch crucible is prepared first by washing the asbestos with 10% NaOH solution, followed by hot alkaline tartrate solution, and finally neutralized with HNO_3 then dried for thirty minutes at 100°C, cooled and weighed.

The milligrams of dextrose are then computed from Munson and Walker's table, and this in turn converted to starch by multiplying by the factor .9. (The Munson and Walker table may be found in "Methods of Analysis" American Association of Official Agricultural Chemists.)

(2) Volumetric Thiosulfate Method:—

The copper oxide on the filter is dissolved with 5cc. of warm 1/1 nitric acid, and the filtrate caught in the flask with the aid of suction. The filter is washed well with boiling water. The contents of the suction flask are then boiled for one minute, and exactly one cc. of NH_4OH (Sp. gr. 0.9) is added, and the solution boiled again for one minute. It is then cooled to room temperature by means of running cold water. 10cc. of a 30% postassium iodide solution are then added and the liberated iodine titrated with standard sodium thiosulphate solution. When the iodine color has practically disappeared one cc. of freshly prepared 1% soluble starch solution is added. The titration is continued until the color due to the free iodine has vanished—i.e., the blue color changing to a faint lilac.

The sodium thiosulfate is standardized by dissolving 19 grams of the crystal in one liter of CO_2 free distilled water. .2 grams of copper foil are weighed out and dissolved with 5cc. of 1/1 nitric acid by warming slightly. After diluting to 500cc., the solution is boiled to expel the red fumes, and the procedure continued as above beginning with "exactly one cc. of NH_4OH (sp. gr. 0.9) is added."

After multiplying the titre by milligrams of copper per cc. of sodium thiosulfate, the milligrams of dextrose present is then computed from Allihn's table for the determination of dextrose (Methods of Analysis, A. O. A. C. P. 454, 1925).

(3) Volumetric Permanganate Method:—

The filter containing the washed cuprous oxide is trans-

ferred to a beaker and trituated with hot water; the crucible being finally washed with 50cc. of a hot saturated solution of ferric sulfate in 20% sulfuric acid solution. The washings are caught in the beaker containing the precipitate. After the cuprous oxide is in total solution, the latter is titrated with a standard solution of $KMnO_4$,—1cc. of which is equivalent to .01 grams of copper. The standardization of the latter solution is effected by electrolysis.

The principles involved in the above determinations have served as a source for the more recent work done in textile analysis in England.

English Methods

D. A. Derrett-Smith (Jour. Text. Inst. 21, T 583, 1930) in experimenting for the British Linen Industry Research Association has advanced a procedure based on the volumetric permanganate method. In the final titration and n/25 $KMnO_4$ solution is recommended. The disadvantage of his method is that small samples must be taken for analysis, since if the final titre exceeds 30cc. than there is great liability for error.

Fargher and Lecomber (Jour. Text Inst. 22, T 475, 1931) in research executed for the British Cotton Industry Research Association were of the opinion that an accurate quantitative starch determination was one which was lacking in textile analysis and have presented one based on the volumetric thiosulfate method. We are presenting their method here, more in detail, since it possesses greater accuracy than that of Derrett-Smith as larger samples of textiles containing more sizeable starch contents may be taken for analysis.

A 2.5 gram sample is dehydrated and the percent of moisture computed. It is then placed in a flask, and wet out with 60cc. H_2O by heating to boiling. After cooling, 20cc. of $4N.H_2SO_4$ are added and the flask placed in a boiling water-bath for 2½ hours. The flask is then cooled, and its contents filtered through a Buschner funnel, and the sample washed with 100cc. water. 19cc. of 4N.NaOH are added slowly from a burette to the filtrate, and the whole made up to 250cc. The glucose is then estimated in this solution as follows:—

25cc. of the solution is titrated with N/2 NaOH. The glucose is then determined in a 50cc. portion by adding 25cc. of N/20. Iodine solution, followed by a volume of N/2 NaOH required to neutralize (as determined on 25cc. portion) plus 3.12cc. The alkali is added very slowly. After standing for ten minutes at 20°C the solution is acidified by adding 1.6cc. of $4N.H_2SO_4$ and the excess of iodine titrated with N/20 sodium thiosulfate. A blank is usually run for correction of the final titration. The amount of N/20 iodine consumed by the blank is subtracted from the total cc. of N/20 iodine consumed by the sample.

1cc. of N/20 iodine solution =.00417 grams of commercial starch.

We have dwelt but little upon the enzymic hydrolysis of starch, since we are of the opinion that for this type of determination much more care must be exercised by the use of a diastase. Secondly, the duration of the conversion is considerably longer. Thirdly, the hydrolysis by an enzyme is not as complete as the conversion by an acid. This has found to be true by Fargher and Lecomber (supra), although they did find that the diastase, Polyzime P did produce a 100% conversion. The following mixture was used:—

15cc. of a 1% solution of NaCl, 15cc. of 2 molal sodium acetate (Ph=5), 15cc. of a 2% solution of Polyzime P in .5% NaCl solution plus 1cc. toluene, with an incubation for 18 hours at 40°C.

Author's Method

The method presented by Fargher and Lecomber appears to be the most complete so far, for the quantitative determination of starch. However, we felt that even this method was somewhat lengthy and open to error for a commercial textile laboratory where numerous and rapid determinations are important requisites. To effect a simpler method, the writer has resorted to the chemical methods of physiological chemistry. One of the latter includes a quantitative determination of the amount of sugar (dextrose or glucose) present in human urine, based upon Benedict's modification of Fehling's solution. The principle of this determination is very analogous to that of the glucose determination following the hydrolysis of starch to the reducing sugar, in textile analysis.

Benedict's solution differs from Fehling's solution in that it is much more stable, and does not decompose on long standing. The solution contains potassium thiocyanate in combination with cupric sulfate, and in the presence of a reducing sugar, a white precipitate of cuprous thiocyanate is formed instead of the red precipitate of cuprous oxide as formed with Fehling's solution. In medicine a quantitative Benedict's solution is used—i.e. one in which 25 cc. are reduced by 50 milligrams of glucose. In the titration a white precipitate is formed, and the loss of all the blue tint in the solution indicates a complete reduction. An alkali, sodium carbonate is used with the Benedict's solution, which has the advantage over the alkali hydroxides in that there is less destruction of small amounts of sugar.

The writer has prepared this quantitative solution according to Hawk and Bergeim (Physiological Chemistry P. 69, 1926 Blakeston) as follows:—

Cupric sulfate crystals	18.0 grams
Sodium carbonate (anhydrous)	100 grams
Sodium citrate	200 grams
Potassium thiocyanate	125 grams
Potassium ferrocyanide (5% solution)	5.0 cc.
Distilled water to make up to	1000 cc.

The sodium carbonate, sodium citrate and the potassium thiocyanate are dissolved with the aid of heat in

enough distilled water to make 800 cc. and the whole filtered. The cupric sulfate is then dissolved separately in 100 cc. of distilled water and this poured slowly into the above filtered solution while stirring. The 5 cc. of potassium ferrocyanide are then added, the whole then cooled and made up to 1000 cc. with distilled water. 25 cc. of the resultant solution are reduced by 50 milligrams of glucose.

The following is an outline of the procedure for the quantitative determination of starch in which the above described quantitative solution is utilized.

A 5 gram sample of the material to be analyzed is dehydrated at 105° F. for 2 hours and weighed. It is then cut into ¼ squares and placed in 50 cc. of 2 normal H_2SO_4 which has been previously diluted with 60 cc. of distilled H_2O. The flask is then placed in a boiling water bath for exactly 2½ hours. The contents are then filtered through a Buschner funnel containing an asbestos filter, with the aid of a suction flask. The filter is then thoroughly washed with distilled water, followed by a wash with 10 cc. of 1 normal sodium carbonate solution, then by another distilled water wash. The filtrate is then refiltered through a No. 1 Whatman filter. The total volume in the filtrate is then measured. The filtrate, which does not usually exceed 75 cc. is placed in a 50 cc. burette, which is filled to the mark. 25 cc. of the quantitative Benedict's solution is pipetted into a casserole, and the latter placed on a tripod over a flame beneath the tip of the burette, as shown in Figure 1. Ten grams

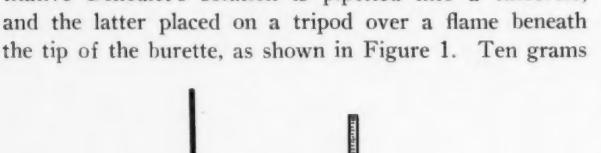

Figure 1.

of anhydrous sodium carbonate are added to the Benedict's solution and the latter brought to a boil and kept at a vigorous boil, while the titration is begun. The end point is reached when a chalk-white precipitate forms and the blue color of the solution disappears entirely. The solution must be kept boiling vigorously throughout the titration. If the white precipitate of cuprous thiocyanate has a tendency to redissolve, 3-4 grams of Na_2CO_3 (dry) should be added to the boiling solution whereupon the precipitate should reappear.

If small amounts of starch are present in the sample, in such a minute quantity that upon hydrolization, it will not reduce 25 cc. of the quantitative Benedict's solution, then the above procedure must be repeated using one-half as much of the quantitative solution. Thusly, in the above description, 25 cc. of the solution has been advised, since in the writer's experience, this is a quantity which would yield titrations which did not give too rapid an end point.

Computations:—

$$w = \frac{.9\ (T \times .05)}{t}$$

$$\% \text{ starch} = 100\ \frac{w}{W}$$

where T = total cc. in filtrate
t = cc. in titer
w = weight of starch
W = weight of the original dehydrated sample

A dilution to one normal H_2SO_4 solution is used for the hydrolysis of the starch in the above determination since previous investigators have found that in two and a half hours on a boiling water bath this concentration of acid will not appreciably hydrolyze enough cellulose to offset the results.

The writer has employed this method of analysis upon shoddy fabrics which had been sized, and checked, the percentages obtained, with those obtained by the volumetric permanganate method of Derrett-Smith with very comparative results.

Known weights of dehydrated samples of pure corn starch and some which had been partially converted to dextrines were placed in solution and the quantitative Benedict's solution used with favorable results. With the dextrines, errors were obtained as high as 10 milligrams, which are certainly not out of line when it must be taken into consideration that when 5 gram samples are taken for analysis, these amount to but .2—.3%.

In a consideration of other carbohydrates present in a finished textile material, it is evident that those which will hydrolyze to form a reducing sugar, if present, will tend to raise the percentage of starch present. Various finishing materials have been subjected by Fargher and Lecomber to a starch determination by their method with the following results:—

	Starch Equivalents
Gum Tragacanth	85%
Gum Tragon	83%
Irish Moss	50%
Gelatin	27%
Glycerine	3%

In size mixtures where a mixture of several finishing materials may be present, the analyst well knows the difficulties of an accurate quantitative determination of each component. The determination for starch in the

(Continued on page 535)

Recent Developments Relating to

Surface Properties of Cellulose Fibers

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THE Colloid Committee of the Faraday Society held a general discussion on "The Colloid Aspects of Textile Materials and Related Topics" at Manchester, England, on September 21st to 23rd, 1932. The twenty-nine papers presented at this meeting were contributed by twenty-five authors from six countries—England, Germany, France, Holland, Switzerland and the United States. Although unable to prepare a paper in time for the meeting, I had the great pleasure of being numbered among the foreign guests. Inasmuch as I was the only American guest present (Dr. Sheppard, who contributed a paper was unable to attend) my position was somewhat like that of the American representatives who sit and "listen in" on the various European political and economic conferences—a sort of unofficial scientific observer.

This paper was presented before the Division of Cellulose Chemistry at the Washington, D. C. Meeting of the American Chemical Society, March 26 to 31, 1933.

Your chairman has asked me to report to you the developments at this Symposium on the Colloid Aspects of Textiles which bear on the subject of our present meeting. Rather than to take up each of the relevant papers separately I shall try to give you a composite of the views on cellulose as I got it at the meeting and from subsequent study of the papers and the ensuing discussions. The complete papers and discussions have been published in Part one of Volume twenty-nine of the Transactions of the Faraday Society for 1933.

On the whole there was little presented that was revolutionary or startling in its newness but in many papers new data were offered to support or to test previously published theories and findings. Most of the papers, moreover, embodied a restatement and resumé of these theories and findings and, because the gathering included so many of the foremost workers in the physics and chemistry of fibrous materials, the lively interchange of views and of criticism which followed each paper and which was continued informally in many groups at meals and at other times, made of the meeting a very effective clearing house of thought.

The term "surface properties" which was suggested to me for the title of this paper is as difficult to define as are a good many terms and concepts used in our field of science. I think that colloid chemistry, due to its youth, contains an even greater confusion of terms and concepts than the older branches of science, particularly with regard to the nature of the forces involved. Primary valence is a clear concept in the light of the electron theory, but secondary valence, polar attractions, coordinative forces, associative forces, Van der Waal forces, are terms which overlap in meaning as used in the literature and which set up distinctions that future research will probably reveal as unreal.

So it is also with classical distinctions between phenomena such as that, for example, of *swelling* on the one hand, which involves the enlargement of dimensions, the softening and flexibilizing of a more rigid structure and the retention of (microscopical) homogeneity; as distinguished from capillary imbibition on the other, which is accompanied by none of these three Katz[1] started his discussion of the laws of swelling with this classification and then pointed out that the line between the two is no longer distinct inasmuch as substances of "border" behavior have since been observed in which the order of magnitude of the capillaries is submicroscopic, yet larger than the distance between molecules. At another point he also remarks that "swelling is in many ways analogous to solution."

This I think is a lesson which we must keep ever in mind—that in our field even more than in the older ones we have not yet gained sufficient insight into all the facts to resolve the complicated and fragmentary results of our present observations into the natural simplicity which undoubtedly underlies the whole scheme of colloidal structure.

The "surface" of cellulose with respect to reactivity and absorbability is not the mere geometric surface (which for fibers or filaments of one denier size corresponding to fine cotton or very fine rayon is approximately 3×10^3 cm^2/gm) but rather according to Sheppard[2] (and to Kalberer and Schuster whom he quotes as having obtained a similar value by a different method)

some 10^7 cm^2/gm, which is some 3,000 times as great. I shall therefore spend no time in trying to distinguish surface properties or reactions from other properties but shall begin with the fundamental unit of structure, the long chain particle or "molecule."

On this one point there was quite general agreement (and this is encouraging because it illustrates the remarkable achievement of the past decade in reaching a better understanding of the basic principle of fibrous structure): namely, that the fundamental unit of cellulose structure is the ring formed βglucose residue or β glucopyranose unit first proposed by Haworth and that these residues are strung together by glucosidic oxygen bridges through positions one and four to form long thread-like "molecules" or primary valence chains in which the glucose rings are alternately face up and face down. Everyone who touched on the subject of cellulose molecular structure accepted this concept either completely or provisionally.

Haworth and Hirst[3] offered additional chemical evidence as to the nature of this long chain structure. After complete hydrolysis of a carefully methylated sample of cellulose they were able to detect the presence of tetramethyl glucose and to effect its quantitative separation form the trimethyl glucose. Assuming that the tetramethyl glucose must have been formed from the terminal groups at one end of the cellulose chains, the presence of straight chains rather than endless loops is indicated and the amount of tetramethyl derivative present corresponds to a chain length of 100-200 glucose units. The authors point out that the chemical methods involved in preparing the methylated cellulose may have caused some degree of scission of the original cellulose structure but not very much. This point is one which applies almost universally to all cellulose research. In almost every instance the knowledge we are gaining is of modified cellulose rather than of native cellulose.

In addition to this chemical method of determining the particle size of "molecular" weight of cellulose, data obtained by two other methods which have previously appeared in the literature were offered. Staudinger[4] applied to cellulose and to rubber the method of viscosity measurements which he had previously used with success on polymerized unsaturated compounds and hydrocarbons.

For long chain molecules in solutions sufficiently dilute so that each molecule is free and separated completely by solvent from the others, he finds that the viscosity of equally concentrated solutions is not constant as is the case for spherical molecules but is proportional to the molecular weight (chain length) of the substance.

By the extrapolation of this law which he found valid experimentally up to a molecular weight of 10,000 (chain lengths up to 500 A°) and by means of a calculation for the influence of the six atom ring structure on the simple linear chain he deduces from measurement of cellulose solutions molecular weights of 120,000 (chain length 3900 A°). Büchner and Samwell[5] applied a method of osmotic pressure measurement to the determination of molecular weight of technical acetocellulose in concentrations of from 0.4 to 5.0 per cent in acetone and obtained values for molecular weight between 34,000 and 41,000 with a mean of 35,000.

The various values for molecular weight presented or quoted in the Faraday papers are tabulated in Table 1.

The discussion which followed these papers raised a number of points of criticism and in this discussion and in other papers, notably that of Neale[6], the validity of the concept of molecular weight was challenged. Particle weight is undoubtedly a more approximate term. One of the criticisms directed at the viscosity and the osmotic pressure methods was that the extrapolations from the experimentally demonstrable laws of small molecules to the measurements made on very long chains is unwarranted. Another was that the dilutions used (even by Staudinger who had determined 0.28% as the limiting viscosity below which the long cellulose derivative chains

Table I

DATA ON "MOLECULAR" WEIGHT AND CHAIN LENGTH OF CELLULOSIC MATERIALS
Appearing in Trans. Far. Soc., Vol. 29, Part 1, 1933

Material	*"Molecular" Weight*	*Chain Length in Glucose Rings Angstrom Units*		*Method and Observer*
Cellulose from Linters	20,000-40,000'	100-200		Chemical. Separation of Tetra from trimethyl glucose, Haworth and Hirst, p. 15.
Acetyl Cellulose Tricetyl Cellulose	120,000 103,000		3900 1900	Viscosity Staudinger, p. 26
Technical acetocelluloses containing 53-55.6% acetic acid	34,000-41,000 avge. 35,000	130		Osmotic pressure Buchner and Samuel, p. 38
Cellulose* (linters)	40,000			Ultracentrifuge Stamm, p. 38
Cellulose*	16,000 minimum			Chemical, Schmidt, p. 38
Ramie or cotton*	(24,000-32,000)	150-200		X-ray Diffraction. Mark, p. 7

*These values are mentioned in this symposium although the method by which they were obtained has been described elsewhere.

were in true free solution) were actually much too high with consequent disturbing interattraction between the long chains. The paper of Professor R. O. Herzog[7] of Berlin on a "shaking effect" in cellulose solutions revealed that even at dilutions as low as 0.03% the cellulose derivative chains formed a structure which could be broken down by agitation with air or with steel balls.

A third criticism of Staudinger's results was based on the necessity for rigid straight chains which his argument demanded. Katz offered some X-ray data on solutions to support the idea of rigid rod-like molecules. Mark, Rideal and Adam on the contrary offered observations which indicated that the chains must be flexible and that although they pack into condensed surface films as straight chains, they become more flexible as the concentration is decreased until when isolated in solution they are much more likely to be curled or spiraled.

That cellulose derivatives in solution are broken down to single chains is indicated by the paper of Adam[8] on the spreading of surface films of cellulose derivatives on water and on solutions. Using a modification of the apparatus with which Langmuir studied monomolecular oil films, Adam has extended the work reported in his book[9] to a study of various cellulose ethers and esters. His conclusions from measurements of the area, the surface pressure and the optical homogeneity of thin films of these derivatives are that (a) the derivatives spread completely or almost completely to films one glucose group in thickness. (b) the chains lie with every glucose ring nearly flat on the water. (c) the chains are flexible and may be vibrating vigorously in the plane of the surface at low compressions. (d) the differences in ease of spreading between different derivatives are partly due to different adhesion of the ester or ether groups for water and partly to the lateral adhesion between the chains.

Sheppard[2] mentioned in his paper the work done in his laboratory on the spreading of cellulose esters on mercury which also established the formation of films of molecular thickness. Of his paper which reviewed the results of long study on cellulose structure, chiefly by sorbtion measurements and which therefore represented a very significant contribution to the knowledge of surface properties, I shall not speak in detail because he has covered this work in his own paper today much more ably than I could.

We come now to the most interesting controversy of the Faraday Society Meeting—namely, that with regard to the fine structure of the natural cellulose fibers. The concept of micellar or discontinuous structure of natural cellulose fibers has attained rather widespread tolerance during the last five years, having been supported most strongly by X-ray diffraction work, notably that of Mark in Germany, Katz in Holland and Clark in the United States.

The English school of cotton technologists, however, while granting of course the presence of a discontinuous structure in the various modified forms of cellulose, have come to doubt the necessity for if not the existence of micellae in *native* fibers believing rather that the primary valence chains are as long as the fiber itself which is built up directly from the single chains of glucose units without any intermediate discrete chain bundles or micellae.

Neale[6] summarized a great deal of data on the modification of cotton cellulose and pointed out that modification occurs along two distinct lines which are sometimes confused because they frequently occur simultaneously. One he calls *activation*. This includes the swelling of the cellulose structure by the absorption of alkalies or of hygroscopic salts which can be completely removed by thorough washing, leaving the cellulose with the original empirical constitution but with an increased reactivity, that is, an increase in active mass rather than in intensity or energy level. Activated cellulose shows an increased sorption of water vapor and of bases and an increased rate of degradation under standard treatment with acids or oxidizing agents. X-ray workers have shown that this activation is accompanied by a shifting or turning of the long chains about their respective axes. This is compatible with Neale's view that activation liberates some of the hydroxyl groups from the polar attraction between hydroxyl groups and oxygen atoms of adjacent chains, without breaking the glucosidic oxygen bonds themselves.

The second type of modification is *degradation* which is caused by acids or oxidizing agents and results in an irreversible modification of the properties of the scoured cotton cellulose. Acids cause hydrolysis at the oxygen bridges between the glucose rings. Oxidizing agents cause an oxidation at the same point which tends to produce either aldehydic or carboxylic "oxycellulose" according to whether the treatment occurs in acid or in alkaline solution.

Degraded cellulose shows decreased intrinsic strength, decreased viscosity in cuprammonium solution and increased reducing power as measured by copper or iodine number of methylene blue absorption.

Neale points out at the outset that the exact chemical state of natural cotton cellulose must remain obscure until some adequate process of purification is found which shall be milder than the dilute alkali boil. However, while cotton thus scoured has undoubtedly undergone some modification, he finds that it yields a cellulose whose properties are reproducible and independent of the variety and origin of the cotton and of the exact conditions of the alkali boil.

His conclusion from analysis of the above data is that a micellar structure is not necessary to explain them; that the distinction between activation and degradation is more naturally explained by a continuous but slightly imperfect structure. The weakest point in his argument is the lack of an adequate explanation of the longitudinal periodicity disclosed by X-ray diagrams. He suggests the possibility that these are due to "a rhythmic variation from the perfectly crystalline structure without sharp discontinuities."

In the discussions which followed Staudinger's paper several other workers advanced this same view of continuous longitudinal structure in natural cellulose.

The comments of Peirce[9] were particularly interesting. He recommended a study of the cotton hair itself in order to suggest the right choice between alternative structural hypotheses. His classification of the types of cohesion within the cellulose structure was the usual one, namely:

(a) Primary valence bonds of the chains lengthwise.
(b) Lateral cohesion of the crystalline structure.
(c) Lateral cohesion where the crystalline order is interrupted.

Whereas Mark[10] ascribes the rupture of *all* cellulose fibers, natural as well as modified or regenerated, to the sliding apart of micellae whose mutual attraction laterally provides the tensile strength of the structure, Peirce pointed out a fundamental difference between the tensile behavior of natural and of degraded cellulose and offered an explanation for it.

This difference is that in raw cotton the tensile strength is high and *increases* with increasing moisture whereas in modified cellulose it is lower and *decreases* with increasing moisture. This contrast is graphically illustrated by two curves which I have taken from the literature, one for cotton from the work of Peirce[10] and his collaborators and one for regenerated cellulose (viscose rayon) which appears in Mark's[11] recent book (Figures 1 and 2).

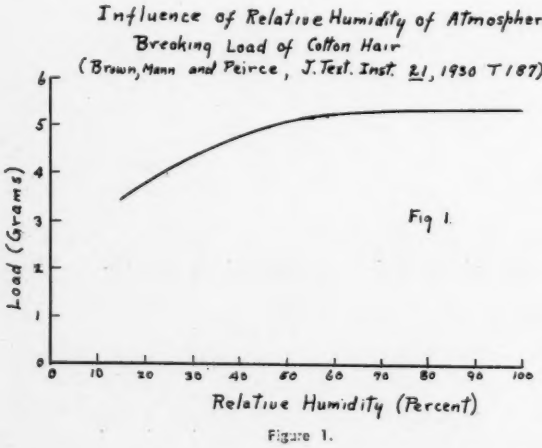
Influence of Relative Humidity of Atmosphere on
Breaking Load of Cotton Hair
(Brown, Mann and Peirce, J. Text. Inst. 21, 1930 T187)
Fig 1.
Load (Grams)
Relative Humidity (Percent)

Figure 1.

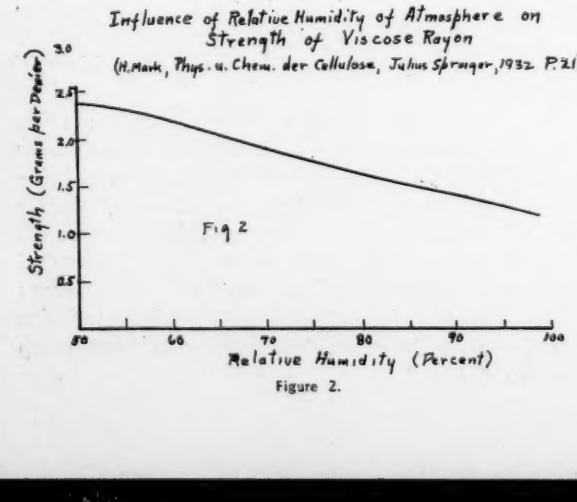
Influence of Relative Humidity of Atmosphere on
Strength of Viscose Rayon
(H. Mark, Phys. u. Chem. der Cellulose, Julius Springer, 1932 P. 21)
Fig 2
Strength (Grams per Denier)
Relative Humidity (Percent)

Figure 2.

Furthermore, Peirce quoted specific data from the paper just cited to illustrate the high intrinsic strength of normal natural cellulose. By observing the shape of cotton hairs before and after breaking he found that a large number of single hair breaks occur at points of abnormal fiber structure. The remaining breaks which are representative of the normal natural cellulose structure give much higher than average figures. Thus for the average of 200 breaks of millimeter lengths of *normal* portions of a sample of cotton he obtained 7.8 g. strength or a breaking length of 45 kilometers as against only 2.6 g. or 15 kilometers for the average of centimeter lengths of seventy-two hairs which contained obvious abnormalities. Comparative tests made on a sample of viscose rayon at the same relative humidity showed for an average of fifty breaks a breaking length of 13 kilometers. Finally he noted (in the same investigation) that the two types of cellulose give diametrically opposite stress-strain curves. These curves show that the extension-load ratio *decreases* with increasing load for cotton and *increases* with increasing load for viscose rayon, i.e., the cotton curve is slightly concave and the rayon curve decidedly convex to the extension axis.

At the Faraday meeting he advanced as the explanation for this fundamental difference in behavior the thought that in natural cotton the tensile strength is due to the first of the three types of cohesion, namely, the rupture of the chemical bonds of the molecular chains themselves which extend the whole length of the fiber. Increasing moisture content acts as a lubricant to loosen the lateral adhesion between chains and so improves the strength by equalizing the stress distribution. The extension-load ratio decreases with increasing load because as the chains straighten out they settle down to share the burden better.

In modified cellulose on the other hand where the continuous chains have been broken down into shorter units Peirce agrees that Mark's explanation of strength in terms of the third type of cohesion, namely, lateral cohesion where the crystalline order is interrupted, holds. Increasing moisture weakens this lateral cohesion and hence lowers the tensile strength. The extension load ratio increases with load because extension in this case is really due to internal viscosity and the viscous flow increases as the lateral cohesion is progressively destroyed.

This Colloid Meeting of the Faraday Society therefore, emphasized a shifting of the focus of discussion from the arrangement of the atoms *within* the elementary cellulose particle to inquiry as to the more exact nature and arrangement of these particles in building up from the fine structure to the fiber structure. The X-ray evidence and the physical evidence on this point have still to be coordinated.

(*Continued on page* 535)

BE IN CHICAGO SEPTEMBER 8 AND 9

PROCEEDINGS OF THE
American Association of Textile Chemists and Colorists

AUGUST 28, 1933

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Aspects of

Boiler Water Conditioning*

By **H. H. MORRISON**
Sales Engineer, The Permutit Company

EVERY engineer knows that scale sludge and mud are formed in steam boilers which operate on natural water supplies. Every engineer also knows that these boiler deposits are troublesome, wasteful, expensive and dangerous. In the past, however, familiarity with these universal conditions led to the opinion that these were necessary evils. This was especially the case when these deposits were not excessively heavy nor hard and when turbinings of the boiler tubes were not unusually frequent.

In the older types of boilers, thin scale deposits were not always such a serious matter as with the lower steam pressures and lower ratings employed, the rates of heat transfer required were not so large. With the modern types of steam boilers, though, due to their higher steam pressures, higher ratings and higher rates of heat transfer, even "eggshell" or "paper thin" scales may cause failure, especially in the highly irradiated sections. Therefore, the correct treatment of the boiler feed water is now not merely a money and labor saving convenience but an absolute necessity.

Hardness in Water

The terms "hard" and "soft" as applied to natural waters are very loosely and inaccurately applied by the public. In fact, the public generally considers a water which is extremely difficult to use as a "hard water" and any water which is less troublesome to use as a "soft water."

*Presented at meeting, South Central Section, May 27th.

Since all natural water supplies, practically without an exception, are hard and form deposits, when used in the steam boiler, it is evident that a different classification is required. Therefore, it is more accurate to term waters that form scale and sludge, when evaporated, "hard waters" and to use the term "soft water" only with those waters that do not form scale and sludge when used in the steam boiler.

The hardness of a water is caused by the presence of soluble compounds of lime and magnesia. Since these compounds are soluble, they are no more visible to the eye than sugar or salt is when dissolved in water. Neither can they be removed by straining or filtering. Therefore, since all natural water supplies contain these soluble scale and sludge forming compounds, it is evident that all of them, no matter how clear, clean and brilliant they may appear to the eye, will form scale and sludge when used in the steam boiler.

Boiler Scale

As the thermal conductivities of boiler scales are very low, ranging in the neighborhood of that of fire brick, they offer a serious resistance to the passage of the heat units into the boiler water. This "misplaced insulation," as boiler scale has appropriately been called, therefore not only wastes heat units but it also raises the temperature of the boiler metal. In other words, in passing a certain quantity of heat units through clean boiler metal at a given rate, a certain differential in temperature is required. But, in order to pass the same quantity of heat units through scaled boiler metal at the same rate, a much higher differential in temperature is necessary.

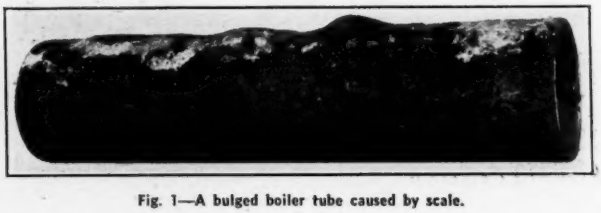


Fig. 1—A bulged boiler tube caused by scale.

This insulating effect of boiler scale therefore frequently results in such serious overheating of the boiler metal that bulging, bagging, burning, or failure of the tubes results. Also, since the higher the rate of heat transfer, the greater is the overheating that occurs, it is apparent that even very thin scales become dangerous when the rate of heat transfer is high.

For example, the maximum safe, continuous working teemperature for boiler steel is considered to be 900° F. Yet in the highly irradiated sections of a modern boiler, only 0.03 inch of scale having a thermal conductivity of 0.75 B.T.U. per square foot of area, per foot of thickness, per hour, per 1° F. temperature difference, may cause temperatures of the boiler steel above this point and consequent failure. Furthermore, since scale with a thermal conductivity as low as K=0.2 may be encountered, it is evident that scale one-third as thick, that is 0.01 inch may cause failure in the highly irradiated sections of the modern boiler.

It is, therefore, apparent that the modern boiler must present as clean a metal surface to the water as possible and that it is not practical to rely on periodic turbinings to keep the scale thickness below the danger line as the factor of safety is too small.

Fig 2—Boiler tube failure caused by a thin scale.

This is especially the case, since the difficulties caused by scale increase not directly but as the square of the rate of heat input. For the rate of scale formation and, consequently, its thickness vary as the rate of evaporation which in turn, varies as the rate of heat input. So, for example, if the rate of heat input is three times as great, scale formed in a given time will be about three times as thick, and, since the temperature elevation caused by a given thickness of scale will also be three times as great, the net result is 3 x 3 or 9 times as troublesome. (Similarly at 4 times the rate of heat input, the difficulties caused by scale will be 4 x 4 or 16 times as great, etc.)

Therefore, the only safe and economical method of handling the scale problem with the modern steam boiler is to prevent scale formation by removing the scale-forming materials from the water by softening it before it enters the boiler. Such systems of water softening yield handsome profits in fuel savings, in the elimination of costly shutdowns and in greatly reduced costs for labor, repairs and replacements.

Water Softening

The four processes used for softening boiler feed waters are distillation, the cold lime soda process, the hot lime soda process, and the zeolite process. The most widely used processes are the last two, namely, the zeolite process and the hot lime soda process. With high bicarbonate waters, a combination process consisting of lime pretreatment followed by zeolite may be used, this being known as the combination lime-zeolite process.

Distillation

In a rather narrow field, where the condensate returns run over 95% and the high cost can be afforded, distillation may be used as a process of water softening. This is accomplished by boiling the raw water, often under reduced pressures, in stills, commonly known as evapora-

tors. Since the mineral substances are non-volatile, they are left behind in the evaporator, while the steam formed is converted into condensate by cooling it in condensers.

While, theoretically, distilled water should form no scale, in practice, some scale-forming materials are found in the condensate and some form of treatment is required to counteract them. These scale-forming materials get into the condensate from two sources. First: by the mechanical carry-over of mineral matter with the steam; and second: by condenser leakage.

The most serious objections to distillation as a water softening process, however, are its relatively high costs, both for equipment and for operation. This, naturally, varies greatly in different localities but an average total cost in eight plants in various locations was 62 cents per thousand gallons of distillate, which is 10 to 12 times the average total cost of zeolite or hot lime soda treated water. Distillation is only practiced, therefore, where condensate returns are very high and, consequently, the amounts of makeup are very low.

Where distillation is practiced, the scale problem is transferred from the boilers to the evaporators. Scale forms rapidly on evaporator coils. By suddenly cooling the coils, some of this scale cracks off but it has been found that such cleaning methods are unreliable and wasteful. It is therefore becoming common practice to soften the water being fed to evaporators. This eliminates scale formation in the evaporators, results in higher evaporative capacities, eliminates mechanical or acid cleanings and reduces labor, repairs and replacements.

Cold Lime Soda

The cold lime soda process is carried out by adding properly proportioned charges of lime and soda ash to the cold raw water; allowing the precipitated sludge (formed by the action of the chemicals on the hardness) to settle for four or more hours; and then filtering. The precipitated sludge consists mainly of calcium carbonate and magnesium hydroxide. These compounds possess a low degree of solubility, so the bulk of the hardness (plus the lime added in the process) is removed by the settling and filtration.

The hardness of the filtered effluent, however, depends upon several factors, such as the accuracy of dosage, the excess of chemicals added, the settling period, the temperature of water being treated, whether or not a mechanical agitator is used, whether or not a coagulant or other chemicals are used, etc. With the excesses of chemicals commonly employed and with the use of a coagulant, the effluent usually has a hardness of 3 to 5 grains per gallon. With excesses of chemicals up to as high as 10 grains per gallon, as used in railroad practice, the hardness of the effluent may be somewhat less than one-half of the above figures.

Hot Lime Soda

The hot lime soda process uses the same chemicals—lime and soda ash—as the cold lime soda process described above, but differs in that it is carried out at or near the boiling point; that the equipment employed is more compact; and that the degree of softening obtained is greater. Briefly, the hot lime soda process, like the cold lime soda process, depends for its action on the fact that the compounds calcium carbonate and magnesium hydroxide possess a low degree of solubility. By adding properly proportioned amounts of chemicals to the raw water, the calcium is precipitated as calcium carbonate and the magnesium as magnesium hydroxide.

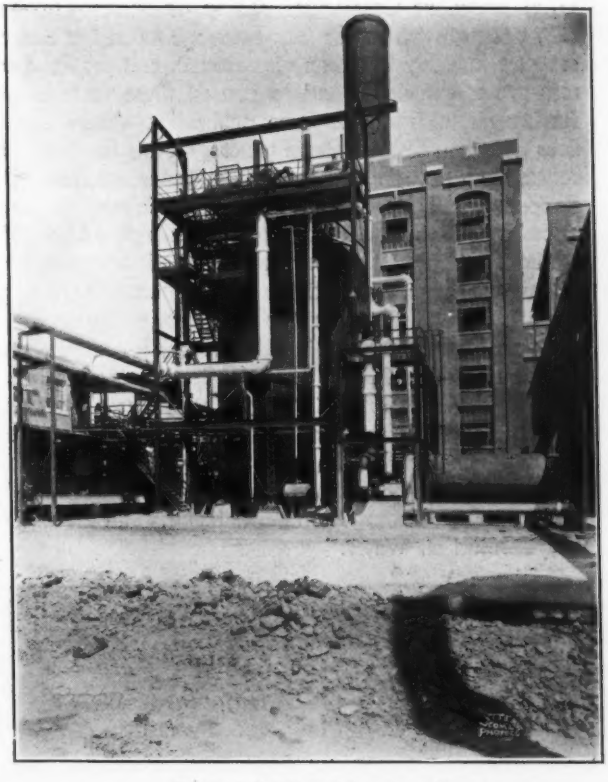


Fig. 3—A Hot Lime Soda water softener.

While these reactions proceed slowly in the cold, they proceed rapidly at temperatures near the boiling point in accordance with the well-known rule that the speed of chemical reactions approximately doubles for each 18° F. rise in temperature. Precipitates formed in the cold also tend to be finely divided and difficult to settle. Precipitates formed hot are larger in size and settle much more quickly especially since hot water is less viscous than cold water. With the hot process type of equipment, it is therefore possible to use settling tanks which are one-fourth the size of the tanks required with the cold process.

With both the cold lime soda process and the hot lime soda process, it is necessary to add excesses of chemicals, but a lower hardness may be obtained with smaller excesses of chemicals with the hot process than is possible with the cold process. With the usual excesses of chemicals employed, the filtered effluent from the hot lime soda process contains between 1.5 and 2.0 grains of hardness per gallon.

Zeolite Process

The simplest method for removing the hardness from a water supply is by the use of the zeolite water softener. Relating to the growth of the zeolite water softening industry, we quote from a recent government publication—U. S. Dept. of Commerce, Bureau of Mines, Bulletin 328, "The growth of the base-exchange or zeolite water-softener industry has been phenomenal, and several factors are responsible"—and as one of these factors, we further quote from the same publication—"Zero water does not form scale in steam boilers, so this has led to a constantly increasing utilization in boiler plants, both stationary and locomotive, particularly in the modern plants with high rates of evaporation at high pressures."

The most interesting property of zeolites is the one of base-exchange, on which their use in water softening depends. While this property was discovered by Thomas Way, an English chemist, in 1850, it was not until some 25 years ago that Robert Gans, a German chemist, discovered how this property might be utilized in water softening and originated methods of manufacturing zeolites and equipment for carrying out this process. These zeolites he named "Permutits" from the Latin "Permuto," to interchange; the process "Permutizing," and the product "Permutized Water."

Fig. 4—A typical Zeolite water softening installation in a boiler plant.

Briefly, when hard water is brought into contact with active or sodium zeolite, the zeolite takes the hardness-forming bases—calcium and magnesium—out of the water and into its structure, exchanging its own base-sodium—for them. For instance, if calcium sulfate is in the hard water, when the water comes in contact with the zeolite granules, the calcium is taken up by the zeolite, forming calcium zeolite, and the sodium goes into the water, forming sodium sulfate. As calcium sulfate is scale-forming and sodium sulfate does not form scale, the net result is that a scale-forming substance has been transformed into a non-scale forming substance.

Similar reactions take place with the other salts of calcium and magnesium present in the hard water, the scale-forming compounds in every case being replaced by the highly soluble non-scale forming sodium salts. This removal of hardness from the raw water is so complete that the zeolite softened water is termed "water of zero hardness" or, more commonly, "zero water." Zero water will not form any scale, sludge or mud when heated or when used in the steam boiler.

Furthermore, these base-exchanging reactions are reversible. So, when a zeolite has exchanged its sodium for calcium and magnesium, it can be restored to its original condition by treating it with a solution of common salt. This is termed "regeneration." What happens during regeneration is that the sodium in the salt solution goes into the structure of the zeolite and the calcium and magnesium go into solution in the forms of the highly soluble calcium and magnesium chlorides. These with the excess of salt, all in solution, are washed to waste, leaving the zeolite in its original active sodium state, ready to soften a further equal quantity of hard water. These alternate softening runs and regenerations may be repeated an indefinite number of times as the wear and tear on a correctly processed zeolite is very slight, in fact, almost negligible.

As active zeolites are insoluble substances, which react only with the hardness of the water, undertreatment or overtreatment of the water, so common with the lime-soda type of water softener, does not occur. For overtreatment is impossible and undertreatment cannot occur as long as the softening run does not exceed the capacity of the zeolite softener. In the lime-soda type of softener, the chemicals—lime and soda ash—must be added in dosages proportionate to the amounts and composition of the hardness salts present in the raw water. Any error made in the dosage therefore results in either an undertreated or an overtreated water. Such errors in lime soda dosage, furthermore, do not necessarily indicate any laxity on the part of the operator nor any fault in the machine. For the composition of the water may change, often quite suddenly and when this happens, the lag occasioned by the time required for testing the water and adjusting the dosages of chemicals means that a certain amount of water of a different composition has passed through the machine and has been incorrectly treated.

With the zeolite water softener this does not occur, for the zeolite bed reacts automatically only with the hardness of the water passing through it. Variations in hardness and composition do not result in undertreatment or overtreatment and the only effects of a changing hardness are: that if the water has less hardness, a correspondingly greater amount of zero water is obtained between regenerations and, if the water has more hardness, a correspondingly smaller amount of zero water is obtained between regenerations. Thus the water softened, in all cases, is completely softened zero water—never undertreated and never overtreated.

Combination Lime-Zeolite Process

With waters high in bicarbonate hardness, a combination treatment, consisting of lime pretreatment followed by zeolite treatment may be used. This treatment reduces the total dissolved solids and, at the same time, completely softens the water thus keeping the boilers entirely free from scale, sludge and mud.

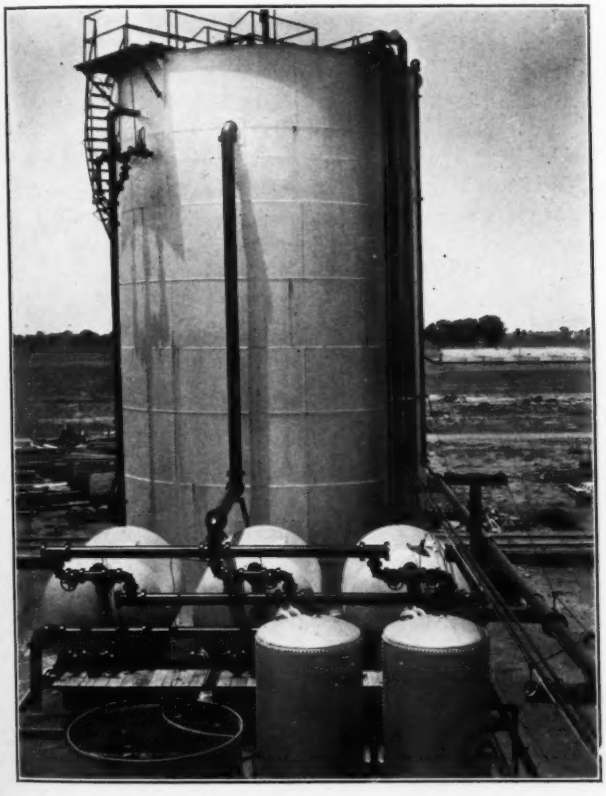


Fig. 5—A combination Lime Zeolite plant.

The combination lime zeolite process has proven especially popular where a water containing a high bicarbonate hardness is used both for boiler feed and cooling purposes. In such a case, the bicarbonate hardness is the scale-former in the cooling jackets while the sulfate hardness is not. This is because the bicarbonates break down when water is warmed, forming carbonates which have a lower degree of solubility; calcium carbonate having a solubility of only 1 grain per gallon and magnesium carbonate having a solubility of 5 grains per gallon. Therefore, these substances, especially the calcium carbonate, form scale in the cooling jackets.

On the other hand, the sulfate hardness does not form scale under such conditions, unless the cooling water is greatly concentrated by evaporation in reuse, because calcium sulfate has a solubility of about 100 grains per gallon at the temperatures employed and magnesium sulfate has a solubility of well over 20,000 grains per gallon.

So, by removing the bulk of the bicarbonate hardness by means of lime pretreatment and then nearly neutralizing the remainder with sulfuric acid or nitre-cake, a water which is practically non-scaling in the cooling jackets may be produced. This water, of course, would not be suitable for boiler feed as, under boiler conditions, the solubility of calcium sulfate is only from 1 grain to 5 grains per gallon, depending on the steam pressure employed and the salts present in the boiler salines, and this is greatly aggravated by the concentration taking place in the boilers. Therefore, to avoid sulfate scale deposits being formed, the lime pretreated water is completely softened by passing it through zeolite water softeners before being used in the boiler.

Type of Water Softener Required

For stationary boiler plants, the cold lime soda process of water softening, due principally to the higher hardness of its effluent, may be ruled out and a choice made between the zeolite process, the hot lime soda process, the combination lime zeolite process, and, providing the make-up water constitutes only an extremely small percentage of the boiler feed water, distillation. This choice well depend on a number of factors. The principle ones are the total hardness and the composition of the raw water; the uses to which the water is to be put; the amounts of chemicals required and their local costs; the quantities and costs of salt; and local facilities, operating conditions, personnel available, etc. These various factors should be determined by means of a careful engineering survey including chemical analyses of the raw water supply. Such a survey will reveal which process is best suited to each case.

In general, the zeolite process is the most widely used (over 9,000 boiler plants in this country now use zeolite softened water); the hot lime soda process and the combination lime zeolite process are of value with waters whose bicarbonate hardness (temporary hardness) is relatively high; and distillation is of very limited applicability, being of use only where the condensate returns constitute over 95% of the boiler feed water.

Economies Effected by Softened Water

By correctly softening the water supply, scale and its attendant troubles and expenses are eliminated. Therefore, boiler maintenance costs are kept at a minimum; fuel is used more efficiently; labor costs are reduced; and repairs and replacements become only a small fraction of what they were formerly.

While the savings that will be realized from such equipment will, of course, vary depending on the hardness of the raw water supply, the amounts of water used, etc., the return on the investment, in general, runs from 40% to over 150% per year. For instance, to give a few scattered examples, one boiler plant saves $3,000 per year which is a return of 100% annually on their investment; another saves $12,290 per year which is a return of 62% on their investment; and a large public utility corporation saves $78,875 per year, which is a return of 116% annually on their investment.

As far as the types and sizes of boilers in which softened water is used, these vary from low pressure heating plant boilers up to the most modern types of high pressure steam generating plants.

The great majority of these use the treated water directly for boiler feed but, in a number of cases, where the condensate returns are high enough to make the use of distilled water feasible, as in central power stations, the treated water is used in the evaporators. The steam pressures employed in these various boiler plants vary all the way from 5 lbs. up to 1,400 lbs. per square inch.

Embrittlement

It has been known for many years that serious cracking occasionally occurs in riveted boiler drums. Various theories have been advanced to account for this and there are two opposed schools of thought. One group of investigators attribute this cracking to faulty workmanship; extensive cold working of the metal; improper shaping, trimming and drawing up of the boiler plates; too free a use of the drift pin; excessive pressures in riveting, etc., which result in setting up undue stresses in the metal during manufacture so that, when subjected to the additional stresses encountered in use, serious cracking finally occurs.

In support of this, cases have been cited where cracking in one or two boilers of a series, operating on the same water, occurred while the other boilers have shown no cracking even under much longer use; cracking of boiler drums during shipment, before ever being put in use, etc.

Other investigators attribute this cracking to high concentrations of caustic soda, with relatively low concentrations of sodium sulfate and sodium carbonate, combined with stresses beyond the yield point of the metal. In order for this to take place, the concentration of caustic soda must reach 100 grains per liter (100,000 parts per million or over 58,000 grains per gallon), and stresses beyond the yield point of the metal must also be present. Such concentrations are, of course, far beyond the concentration of caustic soda that could ever be present in the boiler salines but it is claimed that such concentrations can occur in seams and around rivet holes, especially where caulking is done from the outside. In other words, where there are high caulking edges on lapped seams, resulting in badly fitted plates and where there are high riveting stresses, it is claimed these concentrations can be present.

It is also stated that such action will be prevented if certain salts are present in sufficient proportion in the boiler salines, the theory being that these salts separate out in solid form in the seams or cracks and thereby prevent the caustic soda from concentrating and exerting any harmful action. These salts are termed "inhibitants."

The principal inhibitants are (a) sodium sulfate; (b) sodium sulfate plus sodium carbonate and (c) sodium phosphate.

The A.S.M.E. have therefore suggested as a precautionary measure that certain ratios of sodium sulfate to sodium carbonate be maintained in the boiler water for certain boiler pressures. These ratios, if not present, may be adjusted in various ways, such as by the use of alum, copperas, sodium sulfate, nitre calse or sulfuric acid.

With surface supplies, where coagulation with alum or copperas is employed before filtration, it is often possible to obtain the ratio by regulating the dosage of the coagulent. In other cases, sodium sulfate, nitre calse or sulfuric acid may be used.

The use of sulfuric acid is one that is growing in favor with engineers for ratio purposes because the production of sodium sulfate is accomplished by the reduction of alkalinity. Therefore, the ratio is adjusted at minimum cost and with practically no increase in total solids such as occurs with the use of other chemicals.

Phosphate has recently been recommended after considerable experimentation as an inhibitor for embrittlement and is being widely and extensively used. A certain amount of phosphate in solution has been effective in preventing embrittlement regardless of the sodium sulfate to carbonate ratio. After a hot lime soda plant, phosphate is fed to prevent hard scale formation that may result from the residual 1½ gr. hardness that is inherent in the effluent of such a softener. In addition, an excess is added to get the proper amount of soluble PO_4 as an embrittlement inhibitor. With zeolite, only a small amount is necessary since there is no hardness present to react with the phosphate.

Corrosion

The most prevalent type of corrosion encountered in boilers, heaters, piping, economizers, etc., is that known as "dissolved oxygen corrosion." This is caused by the presence of dissolved air in water. Air, as is well known,

consists principally of a mixture of oxygen and nitrogen. These gases are somewhat soluble in water, the degree of solubility depending both on the temperature and the pressure. As the dissolved oxygen is the corrosive agent, the nitrogen being absolutely inert, this accounts for the term "dissolved oxygen corrosion."

Dry iron in dry oxygen (or dry air) will not corrode. Water must be present for corrosion to take place. Furthermore, this water must be present in the liquid condition. A bright piece of steel or iron exposed to the air does not corrode. But put a few drops of water on it and let it stand in the air and, in a very short time, corrosion takes place. For air dissolves in the water and the dissolved oxygen of this air then corrodes the metal.

Similarly, air in dry steam does not corrode iron or steel. But, if some condensation takes place so that liquid water is formed, then the air will dissolve in the water and corrosion will then occur at the spots where the metal is wet. So, where air is in the steam, especially with superheated steam, it is common experience that the steam lines do not corrode but that the return lines, where liquid condensate is present, do corrode.

The logical way, therefore, of stopping corrosion is to remove the corrosive agent—dissolved oxygen—from the water. Such deaerated water is non-corrosive and, in modern boiler practice, it is recognized that it is infinitely better to have a non-corrosive water than to have a corrosive water and then attempt to produce a partially protective coating on the metal.

The deaeration of water is easily accomplished by boiling it. For while the solubility of oxygen (from air) in water is about 7 cubic centimeters per liter at 60° F., it decreases rapidly with rising temperatures and it is zero in boiling water.

Removing Oxygen with Open Heaters

For the average boiler plant this deaeration is accomplished by properly operating ordinary open or mixing vented feed water heaters of ample size. It is only necessary to heat the water to the boiling point corresponding to the pressure at which the heater operates and to vent the heater liberally, so that the dissolved gases, driven out of the water by the high temperatures may escape freely to the atmosphere.

In those cases where the amount of exhaust steam is not sufficient throughout the 24 hours of the day to keep the effluent of the heater at the boiling point corresponding to the heater pressure, it is necessary to introduce live steam into the heater to keep the temperature up continuously. There is no waste in employing live steam for this purpose because the heat added to the water by the live steam is returned to the boiler in the form of hotter feed water.

On the live steam pipe, a thermostatic valve should be installed. This thermostatic valve will open whenever the water falling from the trays is not up to the boiling point and will close when the boiling point is reached. It thus prevents the use of excess live steam and its waste from the heater vent.

The proper venting of the heater is especailly important. There should be enough vents so that local accumulations of non-condensable gases in portions of the heater are avoided. All the vents should rise vertically without any portions that incline downward or even lie horizontal to act as traps and collect condensate which seals the vent and prevents the escape of the liberated gases. Where throttling valves are employed on vents, these valves should be tested frequently to see that the vents are open.

If it is desired to recover the heat in the steam that may be escaping from the vent, a small surface condenser (vent condenser) can be installed on the vent pipe, employing the cold water on its path to the heater as the cooling water. The condensate formed should be drained back to the top of the heater. The non-condensable gases can then escape directly from the condenser to the atmosphere.

The above construction will deaerate the water sufficiently to prevent any corrosion of the boilers proper. If steel tube economizers are employed preceding the boilers and these tubes are not lead coated or otherwise protected from attack by even very small amounts of oxygen, special deaerator equipment may be required in addition to the above to render the water almost completely free from oxygen. This may be done by thermal means or by chemical means, such as by the addition of oxygen absorbing salts to the effluent of the heater.

As a further safeguard, where economizers are employed, the alkalinity may be built up (increasing the pH value) by recirculation of a portion of the alkaline boiler salines through the economizers. This is not a substitute for proper deaeration but is of advantage as a safeguard should dissolved oxygen, by accident such as pump leakage, come through the lines at any time.

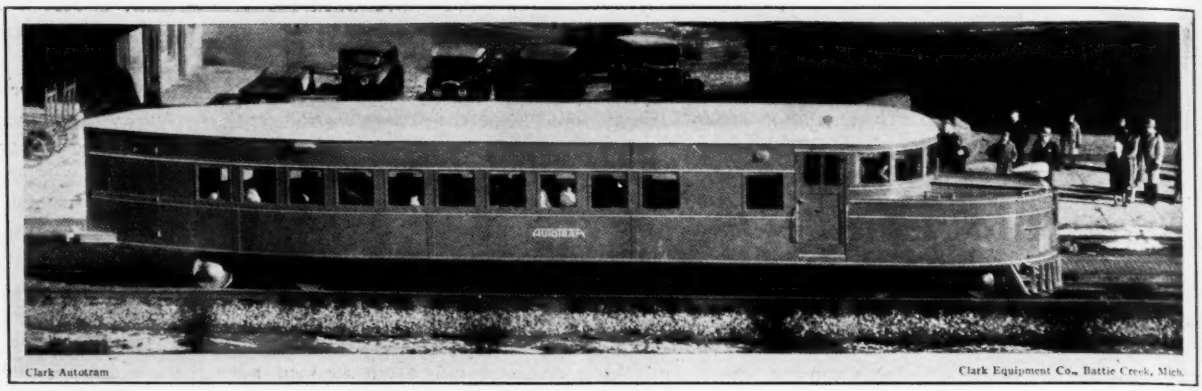
Blow-Off Control

As boiler feed water is evaporated into steam, the salts present are left behind and concentrate in the liquid contained in the boiler (boiler saline). For each particular boiler, under a given set of conditions, there is a limit beyond which it is not safe to concentrate these salts because of the attendant dangers of foaming and priming.

The method used to reduce these concentrations is to blow-off a portion of the concentrated boiler saline and to replace this with fresh boiler feed water.

Boilers now have less water contents per boiler horse power and are driven to higher ratings than formerly. Therefore, not only do concentrations build up more rapidly, but it is also necessary to maintain lower concentrations in order to obtain steam of satisfactory quality. The boilers must, accordingly, be blown off more frequently to control the concentration within these maxi-

(Continued on page (284) 530)



Clark Autotram — Clark Equipment Co., Battle Creek, Mich.

The Autotram now on exhibition at the World's Fair

PATRONS ARE REQUESTED TO FAVOR THE COMPANY BY CRITICISM AND SUGGESTION CONCERNING ITS SERVICE

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I HAVE JUST VISITED THE CHICAGO SECTION THE PROGRAM FOR SEPTEMBER 8 AND 9 IS ARRANGED IN A WONDERFUL SETTING EVERY MEMBER OF THE ASSOCIATION SHOULD DO EVERYTHING POSSIBLE TO ATTEND THE CONVENTION AND THE FAIR IT IS A CHANCE OF A LIFETIME=

ROBERT E ROSE PRESIDENT

Take this copy of the REPORTER with you to Chicago It will serve as a helpful guide at The Convention and Fair

Golfers--Attention

Arrangements have been made for members attending the Convention at Chicago, and who wish to have a round of golf while there, to play at beautiful Olympia Fields Country Club. Play will be over Championship No. 4 Course, a wonderful layout for any golfer to go over. Thursday, September 7th, at 1:30 to 2:00 P. M. will be the starting time.

The greens fee will be only $1.50. The club is easily accessible by Illinois Central Fast Electric from downtown hotels or any south side points.

So that an idea may be had as to how many are contemplating playing golf with the other members on the above date, please write Elmer F. Smith, 820 So. Clinton St., Chicago, Ill. Members signifying their intention to play will be sent a letter giving full details, etc.

Make Your Hotel Reservations Now

Annual Convention A. A. T. C. & C. Chicago, Illinois September 8 & 9

Headquarters--Congress Hotel and Annex

Convention Program

FRIDAY, SEPTEMBER 8

10.00 A.M.

Registration—Room 1102 (Second Floor)

Afternoon

Members are invited to visit:

Corn Products Refining Co., Argo, Illinois; Montgomery Ward & Co., Bureau of Standards. Transportation will be provided.

For those wishing to visit A Century of Progress, we suggest:

Hall of Science ..... 18th St. Entrance
Agricultural, Electrical and Horticultural Buildings ..... 18th St. Entrance
Planetarium ..... 12th St. Entrance
Housing Group ..... 31st St. Entrance
Travel & Transport Building .... 35th St. Entrance
Belgian Village ..... 23rd St. Entrance
Streets of Paris ..... 23rd St. Entrance

Arrangements have been made at Olympia Fields for all who wish to play golf. Leave word at the registration desk if you want a game.

Evening

7:00 P.M.

Dinner—Florentine Room.

Carl E. Bick, Chairman Mid-West Section, presiding.

8:00 P.M.

"How Your Mill Products Stand Laundering"
George H. Johnson, Laundryowners National Ass'n.
Illustrated lecture.

"The Suffering Salesman."
J. D. Sandbridge, E. I. du Pont de Nemours & Co.

"Chemistry in Merchandising."
B. H. Harvey, Director, Montgomery Ward & Co.
Illustrated lecture.

Entrance gates to A Century of Progress closes at 11:30 P.M. Exhibition Buildings close at 10:00 P.M., but places of amusement remain open.

SATURDAY, SEPTEMBER 9
Technical Papers

Morning

10:00 A.M.

"The Iodine Number of Wool."
Milton Harris, Research Associate of the A. A. T. C. C.

10:20 A.M.

"Progress of Sanforizing."
Howard D. Clayton, Cluett Peabody.

10:40 A.M.

"Peroxide Bleaching—A Report of Progress."
H. G. Smolens, Buffalo Electro-Chemical Co.

11:00 A.M.

"The Rayon Industry—A Quarter Century of Progress"
Harold D. W. Smith, A. M. Tenney Associates.

11:20 A.M.

"A Century of Progress in the Wallpaper Industry."
J. G. Stott, Jr., Ciba Company.

11:40 A.M.

"A Comparison of Methods for the Estimation of Small Amounts of Copper in Textiles."
Walter M. Scott, G. J. Esselen, Inc.

12:00 M.

Report of Research Committee—L. A. Olney, Ch'm.

Afternoon

2:00 P.M.

"The Relation Between Tensile Strength and Orientation of Cellulose Fibers."
Wayne A. Sisson, University of Illinois.

2:30 P.M.

"Chemical Constitution and Wetting Action."
W. Kritchevsky, Rit Products Co.

3:00 P.M.

"Modern Theories of Sulfonated Oil."
Lloyd H. Davis, National Oil Products Co.

3:30 P.M.

"Development in the Application of Fat Alcohol Sulfates."
Samuel Lenher, E. I. du Pont de Nemours & Co.

4:00 P.M.

"New Possibilities in the Lubrication of Textile Fibers."
Charles B. Ordway, Alabama Polytechnic Institute.

4:30 P.M.

"Uses of Starch Products in Textile Industry."
H. A. Crown, Corn Products Sales Co.

Evening

7:00 P.M.

Banquet—Gold Room.

Vice-President William H. Cady, presiding.

TOASTMASTER: Grover C. Good, President, Globe Knitting Co., Grand Rapids, Mich.

SPEAKERS: Dr. E. H. Killheffer.

Prof. W. H. Spencer, Dean of the School of Business, University of Chicago.

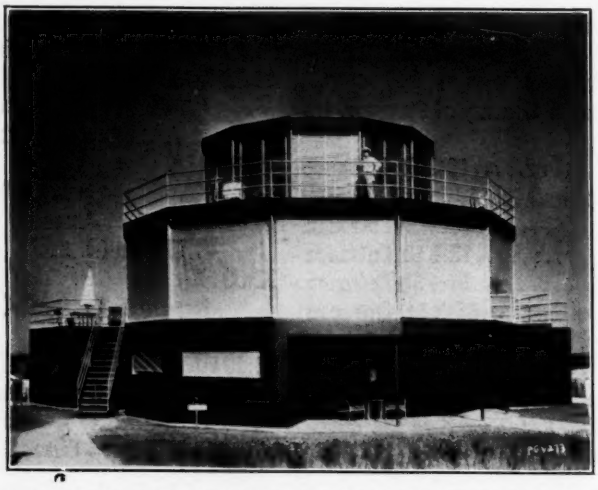
Entrance gates to A Century of Progress close at 11:30 P.M.

What's New and What to do at

Chicago's World's Fair

THE Fair officials say it takes two weeks to see the Fair and if you visit every concession the cost will mount to about $27.00. The committee on publicity has "done" the Fair with reasonable thoroughness and is ready to suggest to the members who come to Chicago in September a program which takes much less time and much less money and yet includes what they believe you will enjoy most.

Starting from the Congress Hotel some morning, walk down to the Art Institute on Michigan Avenue. Admission is 25 cents and the catalogue at $1.00 is a big expense but will guide you to the best in the exhibition, save your time in so doing and be an addition to your book shelf when you get home. Right near the Art Institute you will find a miniature railroad running along the lake, and for ten cents it will take you directly, and in the open air, to the main entrance of the Fair. But before you pay the 50 cents that will admit you through the automatic turnstiles, go into the Field Museum which is right side of the entrance and on the first floor to the left look at the magnificent bronzes of Malvina Hoffman who has sculptured the races of mankind after extensive trips to every country in the world. Admission is free Tuesdays, Thursdays and Saturdays and 25 cents other days. No catalogue is necessary. The Shedd Aquarium is on the spot, too, if you have time. After you enter the gates of the Fair, walk down the Avenue of Flags to the base of the sky-ride. A trip to the tower gives a gorgeous view of the whole Fair and if you are early costs but 25 cents. The Hall of Science is the focal point of the exhibition and now is the time to visit it before you become too leg-weary. The length of your stay in this building will depend on the intensity of your interest in things scientific. The individual exhibits in motion of all the manifestations of the basc sciences are numberless. For the layman one of the most interesting is the transparent man on the lower level. In the Main Hall are the gondola of Piccard's flight into the Stratosphere and the globe in which Beebe descended into the sea.



The all-glass house, built by Century Homes, Inc., in the group of small modern homes in the Home and Industrial Arts Exhibit at a Century of Progress—the Chicago World's Fair of 1933, demonstrates the farthest look ahead that the architect, George Fred Kexck, would cast into the future. Ground floor of the house, including garage, airplane hangar and recreation room has opaque walls. The living quarters and solarium on the top deck have all-glass exteriors, privacy being obtained, when desired, by shades and Venetian blinds. Even the exterior walls are black and opaque glass. There are no windows, all the air in the house being drawn in through air conditioning equipment. Object of the construction is to give the utmost in freedom from housekeeping labor. Decoration of the house by Irene Kay Hyman carries out the scheme with specially designed furniture of metal and wood and the ultimate in labor-saving equipment.

You will find on the upper level of the Hall of Science on the lake side a pleasant place to rest and view the lagoon. If you walk across the bridge and turn North when you get to the island you will be near the Planetarium and here for 25 cents you may sit down in an air conditioned chamber and listen to the lecture while you witness the most amazing and inspiring illusion to be seen in America.

When you come out you will be well rested and ready for a little walking. Stay on the island and drop in as you go South at the Dairy Building, Agricultural Building, Electrical Group and Enchanted Island. Next a trip around the lagoon in a gondola, launch or speed boat will give you a nice view and relaxation and you will be fresh for a trip down the midway. The committee withdraws from an estimate of cost here. At least you can walk through it for nothing. The modern housing group is just beyond the midway and though admission to the modern house reproduced in this article costs ten cents, all but one of the others are free.

Further along on your way South you will find the General Motors Building. Operation on the line had best be seen before five o'clock. Your next stop should be at the Travel and Transport building where there is plenty that is new and interesting. We are leading you toward the pageant of transportation called "Wings of a Century," which is opposite 33rd street. The cost is 40 cents. It is held out of doors and is just about the best show at the Fair. Don't miss it. If you see the 7.00 o'clock show you will be in time to take a bus back to 23rd street and have dinner outside of Leopold's at the Belgian Village. Admission 40 cents, dinner $1.50. It is a good dinner and the floor show is unique.

You are not far now from the sky-ride and if you would like to make a second visit to the tower and look down upon the Fair as it appears at night you will have completed one full day and seen most of what is new at Chicago's World's Fair. A taxi at the 18th street exit will take you directly and cheaply to your room at the Congress.

One day visit to Chicago's Worlds Fair:

Art Institute	$ .25
Art Institute Catalogue	1.00
Miniature railroad to Fair	.10
Field Museum	.25
Entrance to Fair Grounds	.50
Sky-ride tower, before 3.00 P.M.	.25
Hall of Science	Free
Planetarium	.25
Agricultural, Electrical, Dairy Buildings	Free
Boat ride around lagoon	.35
Housing Group, all but two free	.20
General Motors building	Free
Travel and Transport building	Free
Wings of A Century at 7, 8, 9 P.M.	.40
Wings of a Century program	.10
Bus within grounds	.10
Admission to Belgian Village (Dinner outside cafe)	.40
Sky-ride tower at night	.40
	$4.55

Proceedings of the American Association of Textile Chemists and Colorists

UNEMPLOYMENT REGISTER

Members of this association, who are without employment, should forward to the secretary a statement as to their qualifications and experience. This information will subsequently appear on these pages with an identifying key number. Employers are also requested to file with the secretary any vacancies which may occur in their businesses.—A. Newton Graves, Secretary, care Franklin Process Company, Providence, R. I.

Key: A—Laboratory and research; B—Dyeing or printing; C—Finishing; D—Sales; E—Instruction; F—Executive

NOTE. Persons who have obtained employment should notify the secretary at once. Prospective employers may file vacancies either with the secretary or the AMERICAN DYESTUFF REPORTER.

A-1

Education—Ph.B., Brown Univ. '27, P.G. at N. C. State (M.S. this June).

Experience—several years experience as an analytical and research chemist; private research work on sulfonated oils. Twenty-seven years old, married. Will supply references.

A-2

Education—B.T.C., Lowell Textile Institute, 1932; also course in shorthand and typing.

Experience—None to date, interested in quantitative analysis, experimental dyeing, color matching, dye testing and dye identification. Ability to learn quickly and will go anywhere. 23 years old, single.

A-B-1

Experience—over twenty years' experience in the laboratories of various chemical manufacturers, four months' experience as second hand in dye house, familiar with all types of dyes and fibers. Thirty-nine years old. Will supply references.

A-B-2

Education—Lowell Evening Textile School, 1917.

Experience—Five years' experience in hosiery dyeing, full fashioned hosiery of silk and cotton and silk, also men's hosiery containing rayon, wool, cotton and celanese. Several years experience in laboratory work. Has also had experience in jig-dyeing of cotton piece goods, slub and top dyeing.

A-B-E-1

Education—B.S. in chemistry at C.C.N.Y. Working now on M.A. at Columbia.

Experience—7 years as dye tester and color matcher for dye manufacturer; 6 months skein silk and rayon dyer; 4 years textile chemist and dyer for cotton finishing concern; 2 months boss bleacher and 4 years as teacher of organic chemistry and dyeing. Age 38, single.

A-E-1

Education—Ph.D., Univ. of Illinois, studied chemical engineering at Columbia, licensed chemical engineer, New Jersey.

Experience—10 years' experience teaching in colleges, subjects included chemical and textile subjects. Has had broad experience in industrial work including experience in testing materials, research and consulting. Will go anywhere; references..

A-E-2

Education—B.T.C., Lowell Textile Institute, 1933.

Experience—Assistant instructor in chemistry, Lowell Textile Institute. Member of scholastic honorary fraternity.

B-1

Education—educated and trained in chemistry and calico printing in Glasgow, Scotland.

Experience—Has been with large print works as colorist for 13 years producing first class work on cotton, rayon, wool and silk fabrics. References.

B-2

Experience—Boss dyer with one firm for 18 years, divisional supt. at print works for 1 year, in charge of processing and dyeing of cottons and rayons at large bleachery for 6 years. Prefers bleachery in East but will go anywhere. References.

B-3

Experience—Foreman piece dyer for the past 21 years. Can dye the following; celanese, rayon, cotton backs, wool, silk and mixed fabrics. Has knowledge of finishing and laboratory work.

B-6

Education—Graduate R. I. School of Design.

Experience—5 years in bleachery, 7½ years as assistant dyer, 2 years as boss dyer and 3 years as superintendent of dyeing and finishing. Married, 33 years old. References.

B-7

Experience—4 years as assistant to manager in ribbon mill; 2 years as boss dyer on veils, chiffons and silk skeins; 5 years as boss dyer on ribbons and skeins (cotton and silk); 7 years as boss dyer on spun silk (pure dye and fast) resisted colors; last 12 years as hosiery dyer on silk and cotton, silk-cotton, rayon or wool. 50 years old, married. References.

B-8

Education—Chemistry and Dyeing Department, Philadelphia Textile School.

Experience—Eleven years experience as chemist and boss dyer on the following: woolen, worsted and cotton yarn; woolen, worsted and union piece dyes on both ladies and men's wear; wool, cotton, shoddy and mohair raw stock. Age 33, married, will go anywhere. References.

B-D-F-1

Experience—Has held positions as general superintendent of a print and dye works and a finishing company; held a position as boss dyer in a bleachery for 6½ years and as a colorist on 11 printing machines for 3½ years; has held a position as boss dyer for 6½ years with a finishing company and received general training for 3½ years; and has also been dyer in a mill dyehouse. Desires position as superintendent, colorist, dyer or salesman and solicitor.

D-1

Education—Graduate textile course, 1911, Georgia School of Tech.

Experience—Has had experience in all branches of the textile industry but chiefly in sales work. Was at one time in the dyestuff business and later in hosiery manufacturing. Prefers Middle Atlantic or southern states.

F-1

Education—Textile Institute, Alexander Hamilton Inst., Extension work at Brown Univ., working knowledge of German.

Experience—Has had executive departmental work with all types of textiles manufacturers. Acquainted with all types of textile machinery, dyestuff application, laboratory practice, cost methods, and checking methods and processes. References.

BOILER WATER CONDITIONING

(Continued from page (279) 525)

mum limits. Such frequent blow-offs have created the demand for a simple, automatic device in order to avoid troublesome manipulation of blow-off valves and this demand has been successfully met by the continuous blow-off system.

At the same time the continuous discharging of a stream of blow-off water makes it possible to recover the heat contained in the blow-off water by passing it through a heat exchanger in which the make-up water stream (on its way to the heater) is used as cooling water. Therefore, this equipment combines a double advantage; first, it eliminates the troublesome manipulation of blow-off valves and thus makes it easy to blow off the requisite amount to keep below the maximum allowable concentration of salts in the boiler saline, and, second, it recovers the heat in the blow-off stream.

Also, with continuous blow-off equipment, the loads on the heaters or deaerating equipment are much more uniform and, therefore, they function much more steadily and reliably than when intermittent blow-off is practiced. Thus, the use of continuous blow-off equipment results in much better deaeration and, therefore, the corrosion caused by "shots" of imperfectly deaerated water is eliminated. These advantages are so great and this equipment is so simple that its used is rapidly spreading to all classes of boilers.

Before concluding, I have a number of lantern slides which I trust will prove of interest. (Note: A series of slides showing the effects of hard water in boilers and the equipment used in water treatment were shown.)

Allow me to thank you for your attention and, if there are any questions you wish to ask, I will be only to happy to answer them.

Calendar of Coming Events

Annual Convention, Congress Hotel, Chicago, Sept. 8 and 9

* * *

Meeting, South Central Section, Andrew Johnson Hotel, Knoxville, Tenn., Sept. 30

AMERICAN
DYESTUFF
REPORTER

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Managing Editor

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Vol. XXII August 28, 1933 No. 18

LAST NOTICE

AS this is the last issue of the Reporter preceding the Annual Convention of the American Association of Textile Chemists and Colorists, we wish to again urge the members to make all possible efforts to be present. We can assure you that it will be well worth your while. We call your attention to the message of the president of this Association, Robert E. Rose, which appears in the "Proceedings," urging all members to attend.

We also call your attention to the program of technical papers which appears elsewhere in this issue and when you read it over we are sure that you will agree with us that it represents as good a program as we have had in any other year.

Inasmuch as the Convention is being held in September this year, rather than in December as is usual, all members who attend the Convention will have the added advantage of visiting the displays at the "Century of Progress" and this in itself is well worth the time and expense involved.

We congratulate the various committees who have handled the details in preparing for the meeting and hope that the members will show their appreciation by making a special effort to be present.

The Congress Hotel has been chosen as headquarters for the Convention and members are urged to make their reservations now for the length of time they wish to spend in Chicago. For members desiring accommodations elsewhere we have published in previous issues the names of persons and organizations to whom they could write to make the necessary arrangements.

Again we urge you to attend your Annual Convention and enjoy the exhibits of a "Century of Progress."

LABOR AND THE NRA

IF all men were fair and reasonable human beings all adjustments on old contracts for textile goods would now be completed, and the market would be set for a test of the higher prices quoted on new business. If all men were fair and reasonable human beings every industry in this country would now be operating on a code basis in conformity with the Recovery Act, affording opportunity for a reasonably quick test of its practical operation. Men being what they are it is inevitable that there should be waste motion, waste time, attempts at chiseling, unnecessarily exaggerated inequalities.

Even under the best of circumstances a program involving as drastic changes as those made necessary by the NRA could hardly be expected to work smoothly from the beginning. Adjustment to the new order involves wrenches and dislocations, physical and mental, even for those who are heartily in sympathy with its objectives and who are doing everything they can to cooperate. With these points in mind, destructive criticism of the kind which is now fairly common in sections of the industry, does not appear sound.

It may be that the Roosevelt program will be a complete failure, or that it will not work sufficiently well to be retained for any length of time. There is room for sincere differences of opinion on this score. Merely on the basis of what has been accomplished to date, and not what is promised for the future, it would seem to be good policy for every employer in the country to go along with it whole-heartedly until a fair test has been made.

Much has been said about the labor bias of the Government, the Recovery Administration. Much of what has been said has been distorted out of all proper relationship with the facts, in our opinion. It would be presumptuous to speak for the Administration, but we believe its own labor policy speaks for itself. It may hardly be doubted by any unprejudiced observer that this policy embraces a fair deal for employer as well as for employee. That labor, generally speaking, has not received a proper share of the profits of industry, has been demonstrated over and over again by elementary statistics. It is a reasonable deduction that the present Administration intends to try to arrange things in such a way that labor receives a fairer share. This cannot be construed to mean that it is not aware of the dangers of excesses by labor, and that it does not intend employers to receive a fair deal. We believe the prime purpose of the Administration is a fair deal for everyone, and that many manufacturers in our industry are unduly concerned about the labor "bias" of the Recovery program.

Civil Service Examination

The United States Civil Service Commission announces the following-named open competitive examination:

Associate Dye Technologist

Applications for the position of associate dye technologist must be on file with the U. S. Civil Service Commission at Washington, D. C., not later than September 7, 1933.

The examination is to fill a vacancy in the Customs Service, Treasury Department, for duty at New York City, and vacancies in positions requiring similar qualifications.

The entrance salary is $3,200 a year, less a deduction of not to exceed 15 per cent as a measure of economy and a retirement deduction of 3½ per cent.

Competitors will not be required to report for a written examination, but will be rated on their education, experience, and fitness.

Applicants must have had certain specified education and experience.

Full information may be obtained from the Secretary of the United States Civil Service Board of Examiners at the post office or custom house in any city, or from the United States Civil Service Commission, Washington, D. C.

Mechanical "Hand" Developed by Bureau of Standards to "Feel" Cloth

Two instruments have been developed recently in the textile section of the Bureau of Standards for the evaluation of certain of the physical attributes of cloth that affect the sensations which contribute to "handle" and "drape." One is called the flexometer, the other the compressometer. The "handle" or "feel" and the "drape" of fabrics are of importance to the user of textiles; for example, in clothing and home furnishings, as well as to the textile designer, and to the textile-finishing mill, which must produce fabrics having a given "handle" or "drape."

The flexometer provides a means for measuring the flexural attributes of cloth, paper, sheet rubber, and similar materials. These quantities are related to the stiffness and creasability of the cloth. The compressometer provides a means for measuring the compressional attributes of cloth and similar materials. These attributes are related to softness or hardness and springiness, as discerned by squeezing the cloth between the fingers.

Descriptions of the flexometer and the compressometer, together with data illustrative of the results obtained with these instruments, appeared in the May and June issues, respectively, of the Bureau of Standards Journal of Research.

Wash Goods Industry's Trade Practice Code Approved

The Federal Trade Commission has approved trade practice conference rules of the all-cotton wash goods industry relating to such practices as false marking of products, secret payment of rebates, favoritism in granting discounts, and discrimination in price by selling cotton wash goods on the basis of f.o.b. New York in some instances and on a basis of f.o.b. point of origin in others. A second group of rules accepted by the Commission as expressions of the trade relate to usurping of styles, to contracts as business obligations, arbitration, and terms of sale.

The full text of the release can be obtained on application to the Federal Trade Commission, Washington, D. C.

United States Tariff Commission Reports on Production of Dyestuffs

Supplementing previous reports on the production of dyestuffs, the Tariff Commission has just released a statement of the production and sales of dyes, other coal-tar chemicals, the noncoal-tar resins and certain barbituric acid derivatives in 1932.

A total production of 71,269,445 pounds of coal-tar dyes in 1932, and total sales amounting to 73,591,374 pounds valued at $32,944,131, or a 15 per cent decrease in production, 14 per cent in sales quantity, and 15 per cent in sales value, as compared with 1931. Production of unclassified and medicinal dyes increased about 82 per cent, while all other groups decreased.

Absorption of Direct Dyestuffs by Cellulose

A report on an investigation of the absorption of direct dyestuffs by cellulose (cotton, rayon, etc.), as conducted by Research Fellows in the College of Technology, Manchester, England, is reported in the July 7 issue of the British publication, "The Rayon Record." Lack of space prevents our including the several important conclusions reached, but the following paragraph describes the conditions under which the experiment was made:

The problem of determining accurately the absorption of dyestuffs by cellulosic materials, notwithstanding its importance, has only recently been solved, due to the discovery that certain solvents (pyridine and water being the most effective for direct cotton colors) will strip the dyestuff without destroying the color. The dyestuff removed is estimated by a colorimeter of the Duboscq type, and a special technique has been worked out for carrying out the dyeing process under strictly controlled conditions regarding the chemical purity of the dyestuff, maintenance of constant temperature, prevention of contamination from vessels used, and the avoidance of evaporation, etc.

England Investigates Synthetic Resin Dyeware

The British dyeing industry has been challenged by the June issue of the Industrial Chemist to investigate the potentialities for the manufacture of more dye and dyestuffs preparations from phenol-formaldehyde resins. It is reported that the dyeing and that dyestuffs manufacturing industries have shown a definite interest in these possibilities, and it is hoped that the products will be given a genuine try-out. (The Rayon Record, July 7, 1933.)

Rayon Dyeing and Finishing-13

By **B. L. HATHORNE**
Consulting Textile Chemist

CHAPTER VII—DYEING AND FINISHING OF RAYON-CONTAINING HOSIERY

(*Continued from page 509, August 14 issue*)

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Discussion of Scouring

Competition between hosiery manufacturers has been so great that manufacturing costs have been reduced to an absolute minimum. This competition has led to the elimination of the scouring operation in most hosiery mills. The bulk of all rayon-containing hosiery today is entered into boiling baths containing both scouring material and dyestuff. The satisfactory results that are obtained by this general procedure, lead one to conclude that other branches of the dyeing industry can advantageously follow the hosiery dyers' example when suitable machines are made available.

The construction, and the nature of the yarns used, in some kinds of hosiery make it absolutely necessary that a scouring operation shall precede dyeing. As examples of such types, we have both ladies' and men's hose containing a large quantity of real silk in the gum. Also rayon hose made from yarns containing a scroop.

Due to the location of the bulk of the hosiery mills in hard water regions, the biggest problem concerning the hosiery dyer, is proper control of his water. The fact that many of these mills have water softening systems does not eliminate hard water troubles—it only decreases them.

Particularly throughout the south, much of the water entering the dye-house is passed through an alum and soda ash softening system, used to precipitate the silt from the water. The alum and soda ash method of treating water is entirely satisfactory when properly controlled. Unfortunately, most plants do not control their water softening systems as carefully as they should. This results in the consumption of extra chemicals by the dye-house, and loss of time due to spotted goods. Alum and soda ash softening systems should be carefully checked up and inspected at least twice a day in order to reduce trouble from this source to a minimum. When improperly controlled, it is possible for appreciable quantities of alum to carry through this system and reach the dye-house, where it causes trouble due to the production of aluminum soaps.

Many of the mills burdened with hard water have reduced their troubles to a very considerable extent by the installation of water softening systems operating on the zeolite principle. Zeolite softening reduces hard water troubles to a minimum, and materially reduces the cost of dye-house operation wherever hard water is encountered.

Zeolite softening systems operate on the so-called "Exchange" method. That is:— Soluble calcium and magnesium salt present in water passed through a zeolite softening system react with the zeolite and are converted to sodium salts.

When such a quantity of calcium and magnesium has reacted with the zeolite that it becomes inefficient it is "Regenerated" by passing a concentrated sodium chloride solution through the system.

It is particularly important that zeolite water systems shall be cared for as carefully as are the dye kettles. There is a tendency on the part of most mills to attempt to run more water through the system than should be run, and to attempt to reduce the time of back washing to a very considerable extent, because one or two trials on a new system appear to be successful. Such mills are continuously encountering troubles due to hard water and in many instances blame their troubles on everything but the improper control of their water softening systems.

Mills afflicted with hard water and unable or unwilling to instal water softening equipment are forced to scour their fabric, whether the scouring is done as an independent operation or in conjunction with the dyeing operation, with sulfonated oils and an alkali rather than with soap. The reason for this is very simple—sulfonated oils form calcium, magnesium and aluminum soaps much more slowly than do sodium soaps. Also the metallic soaps of the sulfonated oils tend to aggregate or coagulate much more slowly than do the metallic soaps of the higher fatty acids. Thus it is often possible to enter oil con-

taining fabric into a bath consisting of a water solution of sulfonated oil in conjunction with an alkali, and to cleanse goods at the boil in this bath without the precipitation of lime and magnesium soap within the bath and on the goods, even though the water contains appreciable quantities of both lime and magnesium salts.

Generally speaking, it is essential that the time of treatment in such baths be reduced to an absolute minimum, as continued processing in the same bath results in the gradual coagulation of lime and magnesium soaps into aggregates of such a size that grease spots or soap spots are formed on the hose.

The extent to which sulfonated oils and sulfonated oils mixed with various organic and inorganic solvents have replaced soap as detergent materials in hard water regions is not generally appreciated or understood outside of these regions. The basic cause of this replacement is:— the lime and magnesium salts of sulfonated oils do not aggregate as readily as do the lime and magnesium salts of soaps.

The materials that must be removed during the scouring operation or by the combined scouring and dyeing operation are:

(1) Oil used to lubricate the rayon prior to knitting.
(2) Mechanical dirt and grease that become attached to the hose during the manufacturing operations.
(3) Gum from real silk in real silk and rayon real silk combination hose.

The nature of the oil applied has been thoroughly discussed in preceding paragraphs. It is removed during the scouring operation by the process of emulsification aided by saponification in the case of oils containing saponifiable matter.

Emulsification is materially aided by the use of solvents in the scouring bath such as cresylic acid, pine oil, benzine, gasoline, etc.

There are many solvent containing scouring materials offered the trade that consist of mixtures of sulfonated castor oil with varying amounts of the above-mentioned and other solvents in which mineral oil is soluble. The use of some of such material is an economic necessity, particularly when hard water is encountered.

The mechanical dirt acquired by hosiery during the manufacturing process is usually of an oily or greasy nature, and is removed by the same treatment that is necessary to remove the rayon lubricating oils. No special treatment is necessary for the removal of mechanical dirt.

The methods of removing gum from the silk portion of silk and rayon hose sounds theoretically impossible to those unfamiliar with the practice. In many instances degumming and dyeing is carried on simultaneously in a single bath—the total time of operation being materially less than the time usually required for the degumming of silk in other fabrics.

It is possible to so materially reduce the time and the amount of scouring material used for silk degumming, in the case of rayon and silk hose, because of the mechanical condition of the fabric. The silk thread is usually very fine (one to three thread) and due to the relatively loose fabric condition as well as to the presence of the rayon yarn which serves to separate the individual silk threads, the silk is in an ideal condition to be degummed. There is nothing to prevent or retard penetration of the scouring materials.

In some instances, real silk-containing hose are degummed, dyed and finished within an hour's time.

"Soap spots," so-called, encountered during the scouring and dyeing operations, are due to the precipitation of metallic soaps in the dye bath, and subsequent aggregation of these metallic soaps; or to the solution of metallic soaps in mineral oil with the formation of a pasty adhesive material that quickly forms into lumps and adheres tenaciously to the fabric. An analysis of soap spots, reveals the presence of:—

(1) A very pasty adhesive material consisting of metallic soaps dissolved in mineral oil.
(2) Undissolved metallic soaps.
(3) Mechanical dirt.

These spots are formed in the scouring bath whenever improperly emulsified mineral oil is present in a bath containing metallic soaps. They can be prevented when these two materials are present in the same bath, by maintaining the scouring bath in such a condition that the mineral oil is always well emulsified. This is most easily and economically done by the use of solvents. Indeed it is often possible to add solvent-containing materials to a scouring bath and prevent the spotting of goods if the "broken" condition of the scouring bath is detected before the lumps of material have assumed large proportions.

The use of a sufficient quantity of mild alkali, combined with a solvent-containing soluble oil scouring agent, will eliminate the formation of these troublesome soap spots.

Light weight ladies' hose *must* be handled in net bags during the scouring and dyeing operations to prevent the formation of seconds due to distortion of stitch by the dyeing machine. Even in the net bags, it is impossible to process some of the very sheer ladies' hose in the old style wooden rotary machines, as the inside of the drum is so rough that some of the hose become caught and thus are torn or distorted during the scouring and dyeing operations. Trouble from this source has been practically eliminated by the installation of modern machinery.

Light weight ladies' hose become very easily tangled during wet processing. In the event that a scouring operation is found advantageous or necessary before dyeing, it is good practice to remove the hose from the machine, extract them, remove the scoured hose from the bags and shake out all tangles before subsequently dyeing and finishing.

Even when all precautions are observed, some trouble is encountered from tangling during the processing of very light weight ladies' hose. When, as sometimes happens, the hose becomes tangled during the dyeing process, it is impossible to obtain proper penetration during the latter part of the process. This results in the production of light irregular bands where the hose were knotted. Luckily

trouble from this source is not very great. Such hose can be successfully stripped and redyed, the only loss to the mill being the redyeing and reboarding charges.

When it is necessary to scour acetate-containing hose, care must be taken that the temperature of the scouring bath does not exceed 180° F. in order that the acetate yarn shall not become delustered by the action of soap or sulfonated oil. Also care must be taken that any solvent added to the scouring bath to facilitate scouring shall not affect the acetate yarn. As many of the solvent-containing scouring materials now in general use consist of mixtures of solvents, we will not here discuss the action of specific trade compounds on the acetate. However, we wish to call attention to the discussion of the action of solvents on acetate given in Chapter III. Also we strongly recommend that the effect of all solvent-containing materials on acetate be carefully determined before said materials are applied to acetate-containing hose on a commercial scale.

As explained in preceding pages the factors affecting hosiery scouring vary so greatly from plant to plant that it is impossible to write a procedure that can be considered representative of the whole. Below will be found two procedures that are successfully used today by mills working under the two-bath process.

SCOURING PROCEDURE

Rayon and Mercerized Cotton Ladies' Hose

(Soft water available)

(Hose oiled with excess amount of low grade rayon oil)

Per 100 *Pounds Goods*

(1) Enter previously bagged goods.
(2) Add 3 lbs. soda ash to bath.
(3) Add 2 lbs. soap.
(4) Add 2 lbs. solvent-containing scouring oil (mixture of sulfonatic castor oil and a solvent).
(5) Raise bath to boil (fifteen to twenty minutes required).
(6) Boil twenty minutes.
(7) Drop bath.
(8) Rinse.
(9) Extract.
(10) Shake out hose to remove tangles.
(11) Rebag hose and hold for dyeing operation.

(To Be Continued)

DETERMINATION OF STARCH

(Continued from page 514)

presence of carbohydrates which will hydrolize to reducing substances falls into this category. There really exists no method with any degree of accuracy in which the starch may be separated quantitatively from the hydrolizable carbohydrate.

In conclusion, we may state that in the foregoing we have attempted to present

(1) a short review of analytical methods for the determination of starch and

(2) a method dependent on the use of quantitative Benedict's solution, which we have taken from the analytical methods of physiological chemistry and have attempted to apply to textile analysis. The writer is of the opinion that either of these methods lead to much greater accuracy, especially where starch may be the only finishing material added and its quantitative determination a requisite.

SURFACE PROPERTIES OF CELLULOSE FIBERS

(Continued from Page 518)

It seems to me that there is possibly an alternative explanation for the high strength and the favorable influence of humidity on the strength of natural cotton, which is worth mentioning. Studies of cotton hair growth[12] have shown conclusively that the hair grows first to full length as a thin walled sac or membrane within which is subsequently deposited shells of cellulose, which daily thicken the fiber wall. This points to the possibility of a decided difference, in structure at least, between this outer envelope and the rest of the fiber wall. If it should be tougher and less moisture-sensitive than the inner cellulose substance then perhaps the tensile behavior of natural cotton might still be explainable on the basis of micellar structure because moisture by swelling the inner cellulose against the resistance which such an envelope might offer to expansion would improve the lateral contact between micellae and hence the strength. Where this enveloping skin is altered or removed by some process of modification, however, sorbtion of moisture would tend to separate the micellae and so produce the observed lowering of strength.

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The Hydrogen Ion Concentration of Hypochlorite Bleaching Solutions

Abstract by
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WITH a glass electrode, George Forrest Davidson has made a study of hypochlorite solutions, which he reports in the May number of the "Journal of the Textile Institute." This paper is a valuable contribution to our knowledge of these solutions, and suggests methods of practical control for adequate bleaching with least injury to cotton.

Other investigators had shown the maximum oxidation of cellulose by hypochlorites to occur at about pH 7, so that importance of pH in bleaching was well recognized. But common methods of measuring pH with color indicators, hydrogen electrode, and quinhydrone electrode were useless in these strongly oxidizing solutions. The glass electrode, in conjunction with a calomel electrode, had been proved suitable, but at first only in connection with an electrometer or other voltage measuring device too delicate for general use.

In various ways this apparatus has now been simplified so that it can be used in the average laboratory. The electrode consists of a glass tube filled with suitable chemicals connected by wire to a potentiometer. This dips in the solution under investigation, as does also a calomel electrode, connected to the other terminal of the potentiometer to complete the circuit. At some point the glass electrode vessel has a wall so thin as to permit minute flow of current. In modern apparatus this thin part has been extended into a bulb or tube so large in conducting surface as to permit use of comparatively simple voltage measuring devices. Davidson amplified his current for measurement, but with equipment now available this is unnecessary.

Up to pH 9.5 the voltage of such a system is a simple straight line function of pH. Where the only metallic ions present are calcium, as in bleaching powder solutions, this simple relation continues up to pH 12.5 or higher. But in the presence of sodium ions, voltage rises less rapidly with pH, and a calibration curve must be constructed from measurements in buffer solutions. With such variations in sodium ion concentration as would occur in bleaching baths, Davidson considers such a curve valid within ± .1 up to pH 10.5.

Davidson first redetermined the dissociation constant of hypochlorous acid by titration of sodium hypochlorite and calcium hypochlorite respectively against hydrochloric acid, thus establishing the validity of H ion measurements by glass electrode in these solutions. From the titration curves it is evident that the pH of the point where either salt is half converted into free hypochlorous acid and where buffer action is therefore greatest, is 7.43. This buffer is unstable, however, in bleaching, because the salt reduces to chloride and the acid to hydrochloric. A solution of the salt alone should drop to pH 7 on reduction, but any trace of hypochlorous acid should cause a much greater drop. Davidson proved this by reducing with hydrogen peroxide a .02 molar calcium hypochlorite solution, and successively similar solutions with the hypochlorite converted in varying degree into hypochlorous acid. In the first case the pH dropped from 9.7 to between 6 and 7, in the others from somewhat lower initial values to below 3.

In his bleaching experiments conditions were complicated by other factors. Contrary to prevailing impressions he proved that atmospheric carbon dioxide has little to do with drop in pH and liberation of hypochlorous acid. The carbon dioxide formed in the bath by oxidation of cotton impurities he found to be of far more consequence. Spent liquors exposed to air lost carbon dioxide and rose in pH.

Samples taken from the same bath after each of a succession of bleaches rapidly lost oxidizing power on standing sealed, apparently through reaction with oxidizable material previously carried into solution from the cotton. Electrically titrated these spent liquors showed accumulation of buffering compounds from bleach to bleach, not only carbonates but salts of some stronger acid, possibly oxalic. They seemed to contain also some chlorinated organic material.

Davidson sums up the hydrogen ion history of the bath as follows. "In the early stages of bleaching by means of sodium or calcium hypochlorite, the acidic products of the bleaching process reduce the pH by neutralizing the free alkali, and the consumption of hypochlorite has no effect. As soon as the equivalence point is reached, however, the action of the acids produced is supplemented

by an effect due to the reduction of hypochlorite. At pH values below 9.7 the buffer system consists of partially neutralized hypochlorous and carbonic acids—the stronger acid produced by the bleaching being completely neutralized at pH values obtained during actual bleaching. The buffer system is acted on by the acids continually being produced by the bleaching process, and it is also modified by the gradual consumption of the hypochlorite in the manner already described, so that the pH gradually falls. The rapid fall in the early stages of the bleach is due to the rapidity of bleaching and consequent rapid formation of acidic products on the one hand, and the relatively small buffer capacity of hypochlorite solutions at pH values between 11. and 8.5 on the other. In the later stages, the rate of fall of the pH is much less, due partly to the slowing down of the bleaching and partly to the relatively high buffer capacity of hypochlorite solutions between pH values of 8.5 and 6.5. After the end of the bleach, when the partially spent liquor is allowed to stand, the effect of the gradual consumption of the hypochlorite on the pH assumes greater importance, but the pH is prevented from falling to the low value which would be attained in the absence of buffering substances by the buffer action of the carbonate system and of the salt of the unknown weak acid which has been shown to be present. The completely spent liquors contain this acid present almost entirely as salt, and carbonic acid present partly as bicarbonate and partly as free acid.

"The free alkalinity of calcium hypochlorite solutions is limited by the small solubility of calcium hydroxide, which is only about 0.04 normal, so that if a bleach liquor is prepared by dilution of a concentrated stock solution, its free alkalinity must be small. This probably accounts, at least to some extent, for the lower pH values obtained in calcium than in sodium hypochlorite bleaches. That some filtering out of precipitated carbonate by the cloth does take place is shown by determinations of the ash alkalinity of the cloth before and after bleaching. As acidic products continue to be formed during bleaching, the calcium carbonate formed during the earlier stages must gradually dissolve, thus exerting a buffer action, but it is probable that the maximum possible buffer action is not shown on account of the slowness of the attainment of equilibrium between the calcium carbonate and the solution. Such a behavior would help to account for the more rapid fall of pH in calcium than in sodium hypochlorite bleach liquors.

"The pH variation in the bleach liquors containing sodium hypochlorite and soda ash is confined to the region above the hypochlorite equivalence point, so that it must be due almost entirely to the action of the acidic products of the bleach and atmospheric carbon dioxide on the carbonate buffer system. The pH at which a carbonate solution 0.1 N in total base is in equilibrium with atmospheric carbon dioxide is about 10, so that at pH values above 10 all the carbon dioxide produced will remain in the solution. At lower pH values it must escape into the atmosphere as fast as it can diffuse out of the bleaching apparatus, and a similar behavior must be shown by calcium and sodium hypochlorite liquors when the pH values at which they are in equilibrium with atmospheric carbon dioxide are reached.

"The results obtained in the three series of bleaches show that when calcium or sodium hypochlorite is used, the pH falls into the region where the attack on cellulose is relatively rapid, but that this can be effectively prevented by using a sodium hypochlorite solution containing 0.5 per cent of sodium carbonate."

WOOL AND FORMALDEHYDE

The writer has come upon a note by S. R. Trotman on the action of formaldehyde on wool. While not quite new, it is believed to be of general interest and not well known.

A patent of over twenty years ago called for the use of formaldehyde in wool chlorinating baths. It acted only indirectly by reducing the amount of available chlorine.

However, formaldehyde has an important action of its own on wool. Wool absorbs it from aqueous solution to an extent which depends upon the concentration and temperature. Part of the formaldehyde is taken up by absorption and can be removed by continued washing, but about 0.6 per cent will remain.

Wool which has been treated with formaldehyde has a decreased shrinkage and felting capacity but the effect is not permanent. In successive washings the condensation product of the wool protein and formaldehyde gradually undergoes hydrolysis until no formaldehyde remains. Then the fabric exhibits its normal shrinkage again.

The first effects are very pronounced. Some stockings were treated in 1 per cent formaldehyde at 60° for an hour, then worked in dilute ammonia to produce hexamethylenetetramine. The hose did not shrink when boiled in soap for half an hour, but did shrink during a second half hour's treatment.

Formaldehyde-treated wool has a high power of resistance to alkaline hydrolysis.

Such pretreatment has been applied to prevent the shrinkage and felting of Cashmere and Botany stockings during scouring and dyeing. The goods react normally to soap and water. When dyeing is started with acid dyes there is at first little affinity, especially for neutral-dyeing colors. When acid is added to the bath the formaldehyde is split off and the color is taken up. The slightly harsh feel is easily corrected by soap and oil emulsion. (Journal of the Society of Chemical Industry *50,* 465T).

BE AT CHICAGO, SEPTEMBER 8 AND 9

Technical Notes From Foreign Sources

Reserves on Wool and Silk

German Patent No. 469,232 (22/XI/'28)—*I. G. Farben-Ind. A.-G.*—German Patents Nos. 432,111 and 448,-847 cover the use of sulfonation products of phenols, for the decreasing of the affinity of wool and silk for acid and neutral dyestuffs. The present patent covers a similar use of the products obtained by sulfonation of rosins, etc. Colophony, for example, after being solubilized by sulfonation, acts in this protective manner. The products can be employed in various ways; for example, a piece of woolen goods with artificial silk effects may be dyed, as to the wool, with an acid dyestuff, as the sulfonated triarylmethane dyestuff from benzaldehyde and ethylbenzyl-m-toluidine-sulfonic acid, this leaving the artificial silk element untouched; and the latter component of the weave can then be dyed with a direct cotton dyestuff, such as the combination of benzidine with 2-naphthylamine-disulfonic acid and J-acid, the bath containing 3% of the "colophony-sulfonic acid" mentioned above. The two-color effect produced is stated to be much finer than is attainable without the use of the protective compound.

Three examples are given.

Developed Dyeings on Weighted Silk

German Patent No. 462,892 (28/VI/'28) (*addition to G. P. No.* 442,607 *of* 21/VI/'25) — *I. G. Farben-Ind. A.-G.*—The original patent covers the application of developing dyestuffs to unweighted silk, by the methods usually employed in Naphthol AS dyeings. The method works satisfactorily when the alkalinity of the padding bath is kept sufficiently low. When, however, the method is applied to weighted silk, the weighting substance of the silk is partly dissolved, partly loosened by the alkali of the padding bath, thus bringing about uneven dyeings as to the dyeing of the silk itself in the strict sense, and causing the formation of precipitates by reaction with the components of the baths, these precipitates depositing (unevenly) upon the goods, and producing smeary, uneven dyeings of the second order. The results are both weak, and so poor that they cannot properly be called even unlevel, but far worse. Further, the silk loses its luster and scroop.

In this extension of the original patent, the avoidance of these difficulties with weighted silk is brought about by addition of soluble silicates, phosphates, etc., to the padding bath. No precipitation occurs in the baths, and the loosening or solution of the weighting is entirely suppressed, the dyeings being entirely satisfactroy.

Soaps, etc., in Acid Dyebaths

German Patent No. 466,420 (20/IX/'28)—*I. G. Farben Ind. A.-G.*—One of the applications of the familiar emulsifying agents. Consists in the addition of such compounds as di-isopropyl-naphthalene-sulfonic acid, or purified sulfite waste liquor, to the dyebath, thus making it possible to dye, say, wool with an acid dyestuff in the presence of free sulfuric acid, without precipitation of fatty acids from the soap or Turkey red oil which may be present in the bath.

Checking Up on Vat Values

Justin Hausner—Monats. f. Textil—Ind. 101, 47 (1932)—Before the introduction of sodium hydrosulphite as a commercial chemical for use in reducing vat dyestuffs, the vatting of such dyestuffs was an art in the old sense of the word; the dyer of indigo, for example, had learned to estimate the progress and success of the reduction by aspect, sometimes by taste and smell (when we recall some of the reducing agents used in the old days, the latter criterion suggests some qualms). Probably an old, skilled dyer found difficulty in instructing an apprentice in the use of the tests which to him were merely matters of instinct. With the introduction of hydrosulphite, the process of vatting became more definite and understandable. It is not too much to say, that, without the use of hydrosulphite, most of the modern vat dyestuffs would be quite worthless.

Hydrosulfite vatting, however, has its pitfalls, and the modern vat dyestuffs encountered their proportion of difficulties when they began to come into general use. The vat must always contain a certain amount of free, unused hydrosulfite, but not too much, as beyond a certain point the excess of hydrosulfite hinders the taking up of the reduced dyestuff by the fiber. The determination of the necessary and of the maximum allowable limits has not been easy. One method which has been largely employed consists in spotting a piece of the so-called Indanthrene Yellow paper with the vat-liquor, and observing the nature of the change from yellow to blue. Another method consists in dipping a clean sheet of glass into the vat, removing it, and observing whether the layer upon the plate is clear and transparent, and how rapidly the layer is oxidized by the air. Each method requires experience, of course. Another means of judging, available only to very skilled dyers, consists in the observation of the scum upon the surface of the vat. Any of these methods is only a rough means of guessing at the truth.

The author has worked out a more exact method, not yet strictly exact, but much more so that any method yet employed, and fairly approximate, when one considers that, in reducing a dyestuff, oxidation on the surface of the bath is always taking place. He employs an instrument called a "Kuepometer" (exactly translated, a "Vatometer"), which makes it possible to measure not only the excess of unused hydrosulfite in the bath, but also the total reductive power of the vat. For example, if one is working with a vat set at 5 g. of hydrosulfite per liter, this ratio is to be designated as the total reductive power of the vat. It is important to maintain such figures (if that figure has been found to be the most suitable one) during the first part of the dyeing, by occasional addition of more hydrosulfite; toward the end of the dyeing, when the greater part of the dyestuff has been taken up by the goods, this total reducing value can be gradually diminished. If it is a case of continuous dyeing, the original value has to be maintained.

The instrument consist of a glass flask, whose neck is jacketed with a layer of cork, to insulate it from the heat of the hand; this flask is fitted with an inset consisting of a ground-in wide tube projecting well into the inside of the outer flask, and closed at the top and the bottom, except in two points; the tip, (prolonged) of a short burette passing through (fused in) the top of this inset and passing nearly to the bottom of the inset-tube, and the inset-tube carrying a small perforation in the side, a little below the ground joint, for equalization of the pressure between the larger flask and the inset. The burette is calibrated to a maximum value of a reductive power of 10 g. of hydrosulfite per liter, the graduation beginning above and proceeding downward.

To use the instrument, a few drops of a foam-producing liquid are placed in the outer flask, then exactly 10 c.c. of the vat liquor, by means of a pipette, the tip of the pipette being placed as near to the bottom of the flask as possible, in order to avoid unnecessary preliminary oxidation of the liquor. If the vat is hot, the pipette is filled completely, and the two ends are at once capped with rubber "policemen," to prevent oxidation of the liquor while it is being cooled by immersion of the pipette in running cold water. The cooled contents can then, after removal of the caps, be run down to the 10 c.c. mark, and the contents run carefully upon the bottom of the flask. The upper part of the apparatus is at once set in (the surfaces of the ground joint being previously moistened to produce an airtight seal); the burette is filled with water to the zero line, the stopcock being open; the stopcock is then closed, and the whole apparatus shaken well. The foam-producing agent generates a foam which materially increases the surface of the liquid in contact with the air of the flask, and accelerates oxidation of the liquor. When the leuco-dyestuff is quite evidently completely oxidized (shown by complete precipitation of the dyestuff, or by complete loss of the color characteristic of the vat-liquor), the burette is again filled to the zero mark with water (presumably, the water previously filling it will have been thrown out by the shaking of the apparatus), and the stopcock opened. Since the oxidation of the standard volume of vat-liquor in the flask will have absorbed a certain definite amount of oxygen, the level of the water in the burette will sink by that volume, and, as the ground joint permits no leakage of air, will sink no further. The value then read off on the burette, at the water level, gives the total reductive power of the vat.

If a weaker vat is being tested, the percentage of error is kept within reasonable limits by using a suitable multiple of 10 c.c., taking account of the difference in the calculations.

The reading is, of course, subject to correction for temperature and atmospheric pressure, the measurement being a gasometric one; but, as the calibration is made for average conditions, the correction is not worth making.

It will be noticed that the value obtained is generally less than the amount of hydrosulphite added would call for. This fact is explained by the varying quality of the hydrosulphite (a substance which can hardly be kept from deterioration) and by the before-mentioned unavoidable oxidation of some of it from contact of the surface of the bath with the air, even while preparing the bath.

Principles of Colorimetry in Practice

J. W. Perry—Farben-Chemiker 125,3 (1932)—"Color can be considered from two different viewpoints, according to whether it is regarded as cause or effect. Upon the chemist is imposed the task of producing artificially certain prescribed colors, of working out corresponding dyeing procedures suitable for industrial use, and of making them practically workable. In such procedures the color is the result of a material synthesis, and different theories have been established or proposed, partly to systematize the experimental work of the chemist, and partly to explain clearly the phenomena met with. Consequently, the color-chemist of today is in a position to produce practically utilizable dyestuffs of almost any desired color. In most cases, the result must pass as an approximation—which according to circumstances will be more or less exact—to correspond with a color which is to be matched. During the process of working out such a problem, and still more so when the dyestuff comes into practical use, the tendency arises to designate the color by accurate symbols, and to fix definitely its relation to other colors. First, we try to fix its characters by means of words, descriptively. It is easy to see how impossible it is to do so with any degree of exactness, when we consider, for example, how absolutely one is dependent upon such an exact instrument as a thermometer to measure the temperature on a given day. The beginning of the development of this, as with any scientific discipline, is always of a qualitative, descriptive nature. Only later on, through the transition to a quantitative status, does a science become exact, a state which

it is the task of every branch of science to become. In order to bring about this progressive development of the branch of science under consideration, the analytic conditions necessary for exact measurements must be brought together, and made the foundation for a quantitative theory."

The principal difficulty in devising an accurate means of color measurement has lain in the fact that not one factor, but three, are involved. Newton was apparently the first to deal scientifically with the subject of color, and Young, in criticizing and extending Newton's theories, also made some very important contributions to the subject. Helmholtz and Grassmann examined the fundamental assumptions of the earlier work, and found them to be confirmed qualitatively through experiment. Grassmann laid down these general rules:

a—Any compound or mixed color must be the same in aspect as the mixture of a definite saturated color with white.

b—If, of two colors to be mixed, one alters regularly, the aspect of the color produced also changes regularly.

c—Colors of the same aspect give, when mixed, compound colors of the same aspect.

Of these, the first two are still held to be valid, but some doubt now exists regarding the third rule.

Since Maxwell's time, the subject has been further exhaustively studied. The present paper, with its valuable theoretical statements and discussions, some points of which have been noted, leads up to a description of a new colorimeter devised by an English physicist, Guild. A description of it cannot be quoted from the paper, on account of its length and great detail; it is sufficient to say that it involves the use of standard filters, prisms, light-source, etc., and that, being manufactured by the firm of Adam Hilger, of London, it is a carefully constructed and reliable instrument. Two cross-sectional diagrams of its construction, and a cut of the assembled instrument, accompany the article.

The paper closes with a resume of the requirements which a colorimeter should satisfy, and which are absolutely requisite, if the measurements made by it are to be regarded as true measurements:

1—The object whose color is to be measured should possess a definite and constant orientation toward the incident light and toward the direction of observation.

2—The illumination of the object should be exactly reproducible qualitatively. The energy-division in the spectrum of the light-source should correspond exactly to a conventionally agreed-upon standard.

3—The determination of the color should be entirely independent of any variable property of an essential part of the apparatus.

a—The effect of possible alterations in the illumination of the instrument is to be eliminated.

b—The method and class of production or mixing of the standard colors for comparison should have no characteristic individual effect upon the results.

4—The comparison of the mixed color with the color to be measured should take place under definitely fixed conditions, under which the variation of area of the retina which is involved, because of its well-known change in sensitiveness to color (even during an observation) should not overstep a certain prescribed limit.

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